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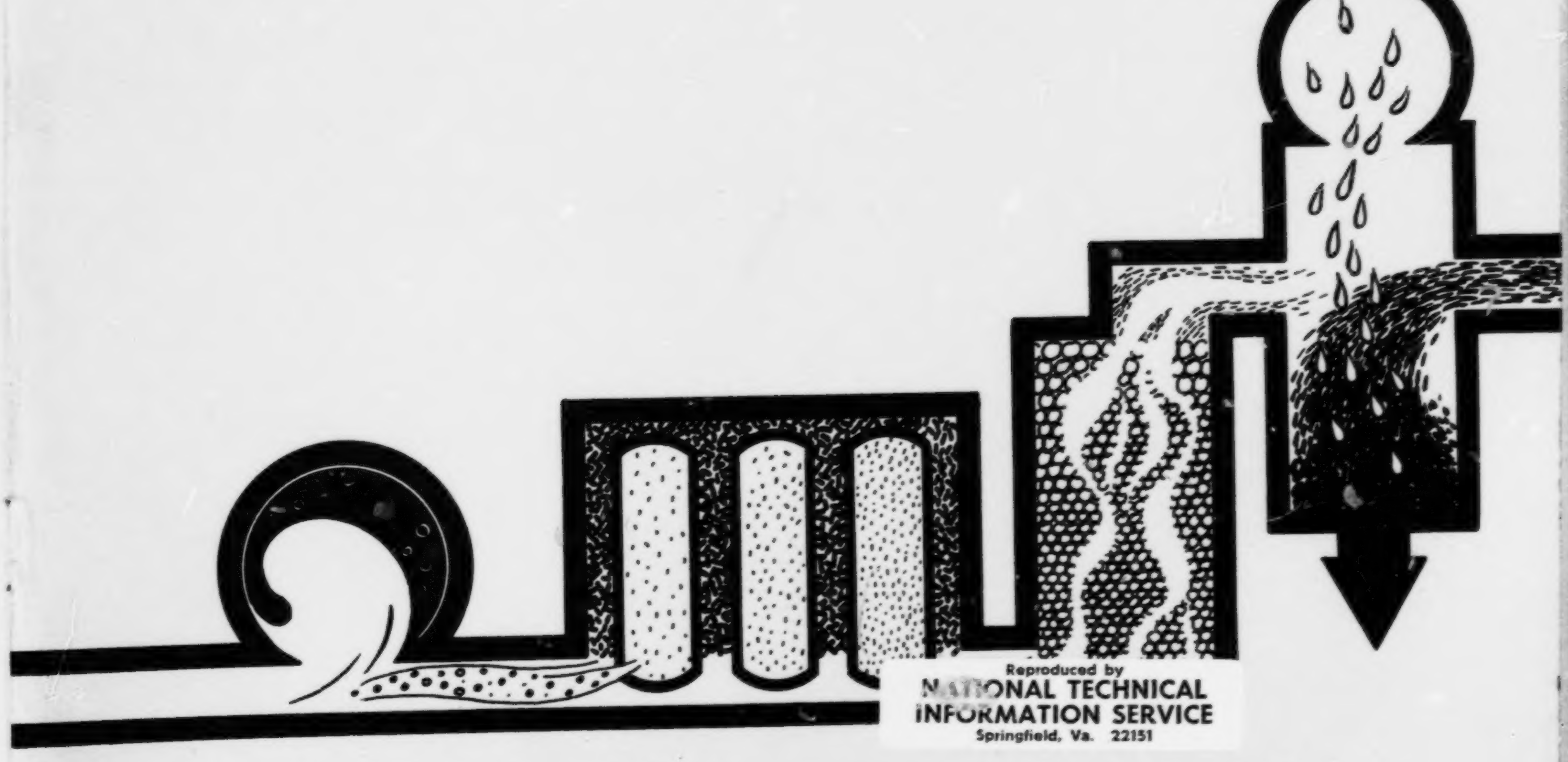
OF
A NEW PHOSPHATE REMOVAL PROCESS



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16. Abstract Two new types of resins were subjected to laboratory evaluations of their technical and economic feasibility for use in phosphate removal. Multi-valent metal derivatives of sulfonic acid resins were found to have good phosphorus capacities. The Iron (III) form of Amberlite 200 strong acid cation exchange resin, for example, exhibited capacities of up to 9.5 mg P/ml of wet resin, and in tests with secondary effluent, a 2.7 mg P/ml capacity was obtained. Exhausted resin was easily regenerable with dilute ferric chloride solution, and after ten exhaustion-regeneration cycles were performed on one sample, no detectable loss of phosphorus capacity was observed. The iron and phosphorus removed from the wastewater and concentrated in the waste brine were subsequently removed from the waste brine by lime addition and settling. A thorough cost analysis including both fixed construction costs as well as operation and maintenance costs, established the price of wastewater treatment by this method as 34.38¢/1000 gal. The second resin type removed only 25 to 35% as much phosphorus as commercially available resins and was therefore dismissed. (Lowry-Texas)

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El Monte, California 91734

for the

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ABSTRACT

A laboratory evaluation was made of the technical and economic feasibility of phosphate removal from secondary effluent by two types of new sorption resins.

The phosphorus capacities of the first type — which included (1) polyhydroxylic esters and amides of various cation-exchange resins (RSO_3-R'-$(OH)_x$ and $RSO_2N(CH_3)$-R'-$(OH)_x$), and (2) polyhydroxylic ethers of styrene-divinyl-benzene copolymers (RCH_2O-R'-$(OH)_x$ — were small, only 25 to 30% of the commercial polyol resin, Amberlite XE-243. Various attempts to increase the capacity of these resins by (1) decreasing the amount of their residual acid functions, (2) increasing their porosity, or (3) decreasing their density, had only minor beneficial effects.

The second type, which consisted of multivalent metal derivatives of sulfonic acid resins, had much higher phosphorus capacities. One such sorbent, the iron (III) form of Amberlite 200 strong acid cation exchange resin, exhibited phosphorus capacities up to 9.5 mg P/ml of wet resin. When this sorbent was evaluated with secondary effluent, a phosphorus capacity of 2.75 mg P/ml of wet resin was obtained.

Regeneration of the exhausted resin was readily accomplished with dilute ferric chloride solutions. On one sample a total of ten exhaustion-regeneration cycles were performed without loss of phosphorus capacity. Iron and phosphorus were quantitatively removed from spent regenerant solutions by the addition of a slight excess of lime and removal of the resulting precipitate by filtration. On the basis of the laboratory results, a phosphorus removal process was designed, and an order-of-magnitude estimate of the cost of phosphorus removal was obtained.

This report was submitted in fulfillment of Project Number 17010 DJA, Contract 14-12-487, under the sponsorship of the Water Quality Office, Environmental Protection Agency.

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SECTION I

CONCLUSIONS AND RECOMMENDATIONS

Of the two broad categories of potential phosphate sorbents investigated in this program, the polyol resins were found to have phosphorus capacities too small to be of practical value; the resin/metal sorbents, on the other hand, had both the capacity and regenerability characteristics required for the attainment of a practical phosphorus removal process.

Based on the laboratory data obtained during the course of this program, a phosphorus removal process can be envisioned consisting of the following steps. Amberlite 200 resin is converted to the iron (III) form by treatment with a 1.0 M ferric chloride solution. Secondary effluent is processed through a stationary bed of this resin on a schedule requiring daily regeneration. Regeneration is accomplished with ferric chloride solution, and backwashing and rinsing utilize stored product water. Waste regenerant is treated with an equivalent amount of lime and returned to the secondary settling tank for removal of the precipitated iron and phosphorus. Using the laboratory data on hand, a cost of 20¢/1000 gal. of water is projected.

This cost could be reduced in several ways. Additional laboratory study should lead to higher phosphorus capacities and reduced regenerant levels. Higher capacities would reduce the capital investment required, by reducing the amount of resin necessary, while lower regenerant levels would reduce the chemical cost.

The above process is based upon removal of phosphorus from secondary effluent containing an average phosphorus content of 10 mg/l, with a product water to contain not more than 0.32 mg P/l. If the process is used for polishing effluent from which a portion of the phosphorus has been removed, a lower cost may result. Such a system could also take advantage of the low phosphorus content (0.07 mg/l) of the product from the sorbent over the first 90% of its capacity.

It is recommended that additional data be obtained regarding the economic aspects of this phosphorus removal process. Such data should include further attempts to improve phosphorus capacity and regenerant levels, as well as studies on the effects of bed depth and flow rates. It is anticipated that such studies would be followed by a pilot scale evaluation to determine the economic feasibility of this promising method for phosphorus removal.

SECTION II

INTRODUCTION

At the present time the cause(s) of accelerated eutrophication and the most effective procedures for its control are being debated. Many — probably the majority — believe that inorganic nutrients (nitrogen and phosphorus) are responsible, and that the removal of phosphate from wastewater is the most practical means of controlling nuisance algal blooms and other growths in aquatic areas. Others maintain that (1) decomposable organic matter is primarily to blame, (2) carbon dioxide is the actual limiting nutrient, and (3) attempts to reduce massive algal blooms by limiting phosphorus in wastewater effluents will not be very effective unless equal emphasis is placed on removing biodegradable organic matter (Reference 1).

Although consensus is lacking as to causes and methods of control, there is virtually no question as to the seriousness of the problem and the genuine need for its solution. The project described in this report was undertaken to develop a more efficient phosphorus removal process based on new kinds of sorbent resins.

PHOSPHORUS REMOVAL PROCESSES

Although a variety of processes have been applied to phosphorus removal (including ion exchange, electrochemical treatment, electrodialysis, and reverse osmosis), the most promising appear to be certain advanced biological treatment methods, chemical treatment, or a combination of the two (Table 1). A third approach, which has been much less studied, is sorption (Reference 2).

Biological Treatment

Biological treatment processes that have been used to remove phosphorus include conventional biological treatment (activated sludge and trickling filter) (Reference 4), modified activated sludge (Reference 5), and algae harvesting (Reference 6). These processes convert soluble phosphorus compounds to organically bound forms in biological cell tissue. Not more than 20 to 40% of the phosphorus normally present in domestic sewage is removed by conventional biological treatment.

Presumably, the removal of phosphorus by adsorption on activated sludge floc, rather than by conversion, overcomes this problem. In this method, the activated sludge process is operated in the dispersed growth phase with a detention time of about 30 to 60 minutes. The organisms containing the adsorbed phosphorus are permitted to floc and are then removed from the effluent and disposed of separately. A variety of removal methods are currently under investigation.

TABLE 1

COMPARISON OF ALTERNATIVE PHOSPHORUS REMOVAL METHODS[(a)]

Process	Removal Efficiency, %	Estimated Removal Cost $/MG	Type of Wastes for Disposal	Remarks
Conventional Biological Treatment	10-30	30-100	Sludge	
Modified Activated Sludge	60-80	30-100	Sludge	
Chemical Precipitation	88-95	10-70	Sludge	Removal efficiency and cost depend on chemical used
Chemical Precipitation with Filtration	95-98	70-90[(b)]	Liquid and Sludge	
Sorption	90-98	40-70	Liquids and solids	Cost based on water treatment costs

(a) Data compiled by Eliassen and Tchobanoglous (Reference 2).

(b) According to W. D. Hatfield, a more realistic figure would be about $105/MG (Reference 3).

Discrepancies in the reported degree of phosphate removal by activated sludge apparently result from changes in composition of microbial protoplasm with different sludge ages and perhaps differences in chemical compositions of wastewaters. It is known that microbial protoplasm is a dynamic, continually changing, material (Reference 7).

Chemical Precipitation

Precipitation of phosphorus in wastewater is usually accomplished by the addition of coagulants such as alum, lime, or iron salts and polyelectrolytes. Commercial processes involving the use of metal ions and polyelectrolytes are also available (Reference 8).

The reactions and removal mechanisms occurring during chemical precipitation are not completely understood. The precipitates are not simple aluminum or calcium phosphates. Cecil has recently reviewed the literature on chemical removal mechanisms (Reference 9).

Chemical precipitation may be carried out as primary or secondary treatment, or as a separate operation. In the primary stage, most of the phosphorus is removed in the primary sedimentation tank. The remaining phosphorus will normally be removed, by conversion, in the biological treatment phase. When precipitation is to be accomplished in the secondary or biological treatment stage, the chemicals are usually added to the aeration tank. The precipitates formed in the biological reactor are removed in the secondary settling tank. By a combination of chemical and biological treatments, the efficiency of phosphorus removal is 80 to 95%. Depending on the chemical dosage, incremental removals of BOD, COD, and surfactant are also achieved (Reference 2).

In some installations, phosphorus is precipitated as a separate operation, following conventional biological treatment. Using alum or lime as a coagulant and precipitant, the coagulation/sedimentation process will remove phosphates to a level of 0.16 mg P/l or less, provided that sufficiently large dosages (200-400 mg/l.) are used.

A promising modification of the chemical coagulation process is the precipitation of phosphorus with a coagulant such as alum on filter or separation beds (Reference 10). Coagulants, coagulant aids such as polyelectrolytes, and pH adjusters are added to the activated-sludge-treatment effluent just before the filter. It is reported that orthophosphate can be reduced to less than 0.32 mg P/l. using alum doses of about 100-200 mg/l. In addition, the BOD is consistently reduced to less than 1 mg/l., and the COD is reduced by about 50%.

Conventional alum treatment for phosphate removal increases the concentration of sulfate ion in solution. A recent report (Reference 11) describes a sorption process in which activated alumina is used to sorb phosphates without any increase in effluent sulfate concentration or change in pH. Regeneration of the alumina is accomplished with small amounts of caustic and nitric acid. Phosphate removal efficiencies up to 98% were attained.

ECONOMICS OF PHOSPHORUS REMOVAL

The costs of various phosphorus removal processes are summarized in Table 1. In order to facilitate the comparison, data on the removal efficiency, estimated cost of treatment, and the form of the ultimate wastes for disposal are given. The wide spread in the cost data for the individual processes reflects the paucity of reliable published information. On the basis of Table 1, it would appear that the best possibility for achieving a high removal efficiency at a minimum cost might be found in some kind of chemical precipitation or sorption process.

Besides the cost of phosphorus removal, however, the costs of ultimate disposal of contaminants must be considered. The quantities of contaminants, both liquids and solids, will depend upon the removal method. For small plants, these contaminants can be handled quite readily in lagoons, sludge drying beds, or sanitary landfills. However, as the treatment plant capacity increases, waste tonnages for ultimate disposal may become a significant problem.

A summary of applicable ultimate disposal methods is given in Table 2. Three generally acceptable possibilities exist: dumping; conversion and dumping; and conversion, product recovery, and dumping. Of the three methods, the last, although the most desirable, is at present the least attainable. A fourth, subsurface injection, is included for comparative purposes only, this method not being considered suitable by current EPA policy.

The cost of ultimate disposal as shown in Table 2 varies over an extremely wide range depending on the disposal method. Because of this wide variation, ultimate disposal methods must be considered carefully; this cost component may be the controlling factor in the choice of removal process or even in the overall feasibility of phosphorus removal per se.

NEW SORPTION PROCESSES

The investigation described in this report grew out of the demonstration in our laboratory that the commercial resin, Amberlite XE-243, has a phosphorus-sorption capacity of about 1 mg/ml, or about one-third of that resin's capacity for boron when determined under similar experimental conditions. The composition of XE-243 may be represented as $R\text{-}CH_2\text{-}N(CH_3)\text{-}CH_2(CHOH)_4\text{-}CH_2OH$; it is prepared by the condensation of a chloromethylated styrene-divinylbenzene (SDVB) copolymer with the polyol, N-methylglucamine. These results suggested that other polyhydroxylic resins might be prepared with higher phosphorus capacity which would be, unlike XE-243, neutral materials with possibly

TABLE 2

ULTIMATE CONTAMINANT DISPOSAL METHODS AND COSTS[a]

Type of Waste	Method of Disposal	Cost[b]	Remarks
Liquid	Soil Spreading	\$0.001-0.3/1000 G	Provisions must be made to prevent groundwater contamination
	Shallow Well Injection		
	Deep Well Injection	\$13-27/1000 G	Disposal site should be available (porous strata, natural or artificial cavities, etc.)
	Landfill	--	Used as a wetting agent
	Evaporation Pond	\$8-64/1000 G	Provision must be made to prevent groundwater contamination
	Ocean Outfall	--[c]	Truck, rail hauling or pipeline needed to transport the wastes
Sludge	Lagooning		
	Landfill	--	Used as a wetting agent
	Recovery of Products	--	Depends on waste characteristics
	Wet Combustion	C.C. \$4-80/GPD[d] O & M \$1.4 to 35/1000 G[e]	Heat value may be recovered for use
	Incineration	C.C. \$10-100/GPD O & M \$5- 55/1000 G	Concentration of sludge is needed. Ash must be disposed of.
Ash	Landfill	\$0.75-1.0/ton	
	Soil Conditioner	--	Depends on waste characteristics

(a) From Eliassen and Tchobanoglous, Reference 12.

(b) Costs vary with plant capacity and land cost; they are based upon volume of waste (i.e., sludge or concentrate) handled, not necessarily on volume of sewage treated.

(c) \$25/ft for 8" dia pipe.

(d) C.C. = Capital cost

(e) O and M = Operation and Maintenance

increased specificity for phosphate. A program having as its objective the investigation of the technical and economic feasibility of phosphate removal from secondary effluents by means of polyol sorption resins was funded by the Federal Water Quality Administration.

The scope of this program was to include:

1. Preparation of a number of microreticular and macroreticular polyhydroxylic resins.
2. Determination of the phosphate capacity of these resins and of XE-243 using synthetic orthophosphate and polyphosphate solutions and natural secondary waste effluent.
3. Determination of the regenerability of the candidate resins (including XE-243) with respect to regenerant levels, recovery of sorbed phosphate, and volume of waste solutions produced.
4. Determination of the stability of the new resins relative to XE-243.
5. Preparation of an estimate of the economic feasibility of phosphate removal by sorption on a polyol resin.

The new polyol resins that were desired for evaluation as phosphate sorbents were esters and amides preparable by the reaction of acylating cation exchangers with polyhydroxyl alcohols or amines.

$$RSO_2Cl + HO\text{-}R'\text{-}(OH)_5 \longrightarrow RSO_3\text{-}R'\text{-}(OH)_5$$

$$RSO_2Cl + HN(CH_3)\text{-}R'\text{-}(OH)_5 \longrightarrow RSO_2N(CH_3)\text{-}R'\text{-}(OH)_5$$

$$RCOCl + HO\text{-}R'\text{-}(OH)_5 \longrightarrow RCO_2\text{-}R'\text{-}(OH)_5$$

$$RCOCl + HN(CH_3)\text{-}R'\text{-}(OH)_5 \longrightarrow RCON(CH_3)\text{-}R'\text{-}(OH)_5$$

Later, polyol ether derivatives from resin quaternary ammonium and sulfonium halides were also investigated.

$$RCH_2S(Me)_2Cl + HO\text{-}R'(OH)_5 \longrightarrow RCH_2O\text{-}R'\text{-}(OH)_5$$

$$RCH_2N(Me)_3Cl + HO\text{-}R'\text{-}(OH)_5 \longrightarrow RCH_2O\text{-}R'\text{-}(OH)_5$$

After a number of different polyol resins had been prepared and found to have disappointingly low capacities, the program was modified to include the preparation and evaluation of two additional types of sorbents: (1) ion-exchange resins containing multi-valent metal ions, where the metal was iron or aluminum; and (2) resins containing silanol (Si-OH) groups.

The rationale for proposing the investigation of these materials was as follows: the removal of phosphate during secondary treatment of wastewater is accomplished by the addition of lime, iron salts, or aluminum salts. The mechanism of removal is generally believed to involve either the formation of metal phosphate or the physical adsorption of phosphate ion on hydrolyzed metal salts. At the present time, the former view is possibly more popular.

Phosphate is also known to be relatively immobile in the soil, although the mechanism or mechanisms involved are subject to debate. Sorption of iron, calcium, or aluminum phosphates may occur on the silicate lattice of clay, or phosphate ion may actually replace hydroxyl in the silicate lattice. In addition, the hydrous oxides of iron and aluminum, which are a major component of soil, are thought to play a role in the fixation of phosphate.

Based on the above facts, it seemed possible that materials with high phosphorus capacity might result if such functions as Fe-OH, Al-OH or Si-OH could be fixed on an insoluble, stable matrix (as provided by a resin). To be of practical interest, the phosphate must be removable from the sorbent, preferably (but not necessarily) without also removing the moiety responsible for binding the phosphate.

When sample compounds were prepared as shown below, the silanol derivative (obtained in 51% conversion) was found, like those of the

$$RCH_2Cl + H_2N(CH_2)_3Si(OEt)_3 \longrightarrow \xrightarrow{H_2O} RCH_2NH(CH_2)_3Si(OH)_3$$

$$RSO_3Na + FeCl_3 \longrightarrow \xrightarrow{H_2O} (RSO_3)_3Fe + (RSO_3)_2FeOH$$

polyol esters and amides, to have a phosphorus capacity much smaller than that of XE-243; the capacity of the sulfonic acid/iron product, on the other hand, was much greater than that of XE-243. Accordingly, the remainder of the original program was spent in studying the sorption and regeneration characteristics of this iron-containing sorbent.

Based on the promising results obtained with resin/iron sorbents during the latter part of the original program, a six-months extension was requested and granted for the purpose of studying phosphorus removal by resin/metal sorbents. The scope of the amended program included essentially the same objectives as the initial program, but was based on the more effective resin/metal sorbents.

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SECTION III

RESULTS AND DISCUSSION

As indicated in Section II, the two major goals of this program were (1) the preparation of a variety of phosphate-sorption resins, and (2) the evaluation of their potential utility as sorbents in an economically feasible phosphorus removal process.

In keeping with the desire to develop ultimately a minimum-cost process, the syntheses undertaken were selected, so far as possible, with a concern for (1) their minimum complexity, (2) the commercial availability of the necessary resin substrates, and (3) the relative ease of preparation of essential intermediates, such as resin sulfonyl chlorides and carbonyl chlorides.

SORBENT SYNTHESIS

Resin Sulfonyl Chloride

As summarized in Table 3, both commercial sulfonic acid cation exchangers and an unsulfonated 1%-crosslinked SDVB copolymer were readily converted to their sulfonyl chloride derivatives by reaction with chlorosulfonic acid. The latter served as both reagent and solvent.

$$RSO_3H + ClSO_3H \longrightarrow RSO_2Cl + H_2SO_4$$

$$RH + 2ClSO_3H \longrightarrow RSO_2Cl + H_2SO_4 + HCl$$

The volume of chlorosulfonic acid required to maintain sufficient fluidity varied inversely with the degree of crosslinking in the resin substrate.

TABLE 3

PREPARATION OF RESIN SULFONYL CHLORIDE

Run	Resin, g[a]	$ClSO_3H$, ml	Temp, °C[b]	Time, hr	Yield, %[c]
36-S	D50W(H), 23	150	80	6	89.5
86-S	A200(H), 25	100	80	6	88.0
122-S	ES-1, 10	90	70	6	96.6

[a] Dry weight.

[b] Prior to being heated, the mixture stood for 16 hours at room temperature.

[c] Based on Cl content.

In preliminary experiments not reported here in detail it was found that (1) reaction did not occur when chloroform was used as a solvent; (2) attempted chlorination of the sodium form of the resin resulted in extensive bead breakage, due perhaps to the precipitation of sodium bisulfate inside the beads; and (3) comparable yields of sulfonyl chloride were obtained fromIR-120 and D50W, but the latter exhibited only an insignificant amount of bead breakage, much less than that shown by IR-120.

Thorough washing of the products with a dilute sodium carbonate solution (see Section IV) was required to remove sorbed sulfuric and hydrochloric acids. A washed product was stable for months, whereas unwashed products developed a hydrogen chloride odor in 2 to 3 weeks, with a consequent loss in chlorosulfonyl content.

Resin Carbonyl Chloride

The conversion of IRC-50, a carboxylic acid cation exchanger (RCOOH), to the acid chloride (RCOCl) was performed using either thionyl chloride or phosphorus pentachloride (Table 4). Preliminary experiments with phosphorus trichloride or phosphorus oxychloride provided only traces of acid chloride; reactions with chlorosulfonic acid under a variety of conditions resulted only in extensive charring.

TABLE 4

PREPARATION OF RESIN CARBONYL CHLORIDE

Run	Resin, g[(a)]	Reagent, g	Solvent, ml	Temp, °C	Time, hr	Cl, %[(b)]
9-A	IRC-50, 10.9	$SOCl_2$, 65.0	None	65-76	9	9.1
18-B	IRC-50, 0.8	PCl_5, 1.8	Benzene, 10	80	4.5	9.1
62-A	IRC-50, 10.9	PCl_5, 46.3	Toluene, 90	110	20.5	10.0

(a) Dry weight.

(b) A fully chlorinated product contains 32.4% Cl.

The chlorine contents obtained indicated a 30% conversion to the carbonyl chloride. However, it is known that thionyl chloride effectively converts carboxylic acids like maleic, succinic, or phthalic to their respective anhydrides, $(RCO)_2O$ (Reference 13). Confirmation of the presence of significant amounts of anhydride was obtained from the infrared absorption spectra (Section 4). The mixed acid chloride/anhydride composition of the products was further confirmed by their reaction with N-methylglucamine (see below), which provided much larger yields of the amide than could be accounted for on the basis of the acid chloride content alone.

ES-1 Copolymer

One consideration that was briefly explored in the effort to obtain sorbents of higher phosphorus capacity was the possible effect of porosity. In order to be able to compare a porous but highly crosslinked resin such as A200 with a porous but low-crosslinked resin, it was first necessary to synthesize the latter, which was not available commercially. A low-crosslinked intermediate would have the additional advantage of greater chemical reactivity. It is of interest in these connections to note that XE-243, as well as a number of known anionic and metal-chelating resins, has a DVB content of only 1 to 2%.

Some typical preparations of ES-1 copolymer beads, made using polyvinyl alcohol and magnesium silicate as suspending agents, are summarized in Table 5. The rate of stirring was found to be the most critical factor in determining bead size.

ES-1 Chloromethyl Resin

Reaction of ES-1 copolymer with methyl chloromethyl ether in the presence of Friedel-Crafts catalysts provided the chloromethyl derivative (Table 6), which was required as an intermediate for the

$$RH + ClCH_2OCH_3 \xrightarrow{\text{catalyst}} RCH_2Cl + CH_3OH$$

preparation of resin polyol ethers. As the extent of chloromethylation increased, the bead color changed from white to yellow, and bead hardness increased. The latter is probably indicative of the occurrence of crosslinking (Reference 14). Zinc chloride was the most effective catalyst (Reference 15).

Resin Polyol Sulfonates

Resin polyol esters were prepared by the reaction of resin sulfonyl chlorides with pyrogallol, mannitol, or sorbitol in the presence of bases.

$$RSO_2Cl + HO\text{-}R'\text{-}(OH)_x \xrightarrow{\text{base}} RSO_3\text{-}R'\text{-}(OH)_x + HCl$$

A preliminary study of the behavior of resin sulfonyl chloride in candidate reaction media had demonstrated the superior swelling actions of DMF and DMSO. Water and pyridine produced only slight swelling, and toluene and triethylamine practically none (Figure 1). DMF was preferred to DMSO because it showed less tendency to cause bead breakage, or to decompose or undergo reaction; furthermore, the complete removal of DMSO from the products was difficult.

TABLE 5

PREPARATION OF ES-1 COPOLYMER BEADS

Run	Water	Styrene	Polyvinyl Alcohol, g	Magnesium Silicate, g	Temp, °C	Time, hr	Rate of Stirring, rpm	Yield of Copolymer, %	
								20-45 mesh	45-100 mesh
141	300	50	2	1	80	6	700	30	20
144	300	50	2	1	80	5.5	800	10	40
150	2100	350	14	7	80	6	900	9	58
222	2100	350	14	7	80	6	750	39	43

TABLE 6

PREPARATION OF ES-1 CHLOROMETHYL RESIN

Run	ES-1, g	Methyl Chloromethyl Ether, g	Catalyst, g	Temp, °C	Time, hr	Cl, %	CH_2Cl, units/ring
124-C	4	40	$ZnCl_2$, 3	24	1	27.2	1.15
				60	2		
136-C	3	30	$AlCl_3$, 2	24	16	2.1	0.12
145-C	3	30	$AlCl_3$, 2	45	16	9.2	0.53

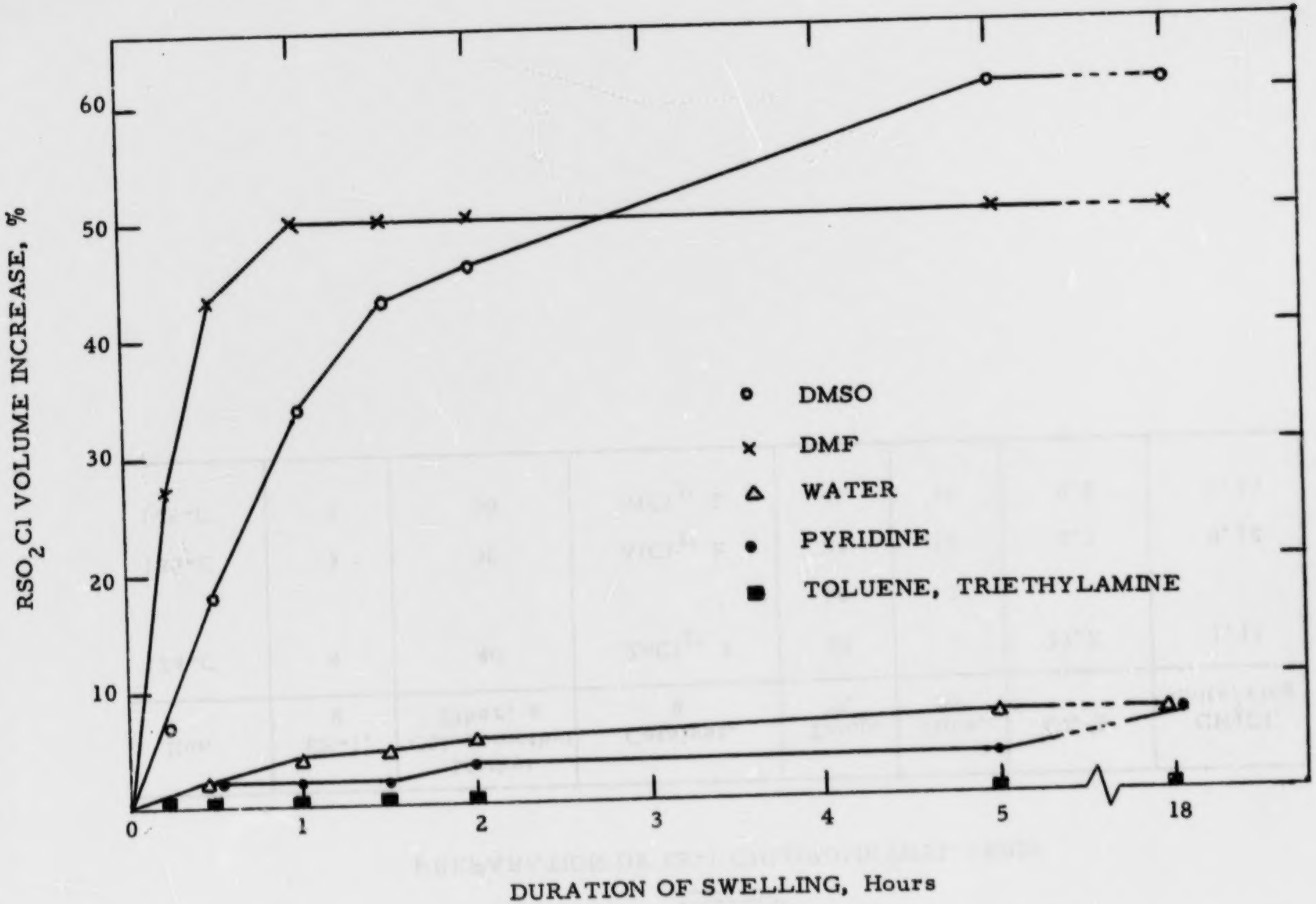

Figure 1. Swelling of RSO_2Cl in Various Liquids

The results of the preparations are summarized in Tables 7 and 8. The pyrogallol ester (Run 77) was obtained in 58% yield (based on weight gain) when prepared in DMF, using pyridine as the base. The sulfur content of the ester, however, corresponded to a much higher yield (Table 8). Other preparations in pyridine as medium and/or at lower temperatures were less satisfactory.

The sulfonate esters of mannitol and sorbitol presented more difficulty. Pyridine was ineffective, and the products obtained using triethylamine in DMF or DMSO were impure. Thus, a 41% yield of ester resulted in Run 77, but the product also contained 4.64% N (Table 8). The absence of odor and the presence of only trace amounts of DMF (as shown by infrared analysis) suggested that the nitrogenous impurity was present as an amine sulfonate salt or as a sulfonamide.

When the reaction was attempted with ES-1 sulfonyl chloride in a dioxane/water medium (Run 142), a pure product was obtained as indicated by its elemental analysis (Table 8). Although the yield based on weight gain was low, the analyses corresponded to a composition that was 45% of the desired ester and 55% of residual sodium sulfonate.

Pure products were also obtained in reactions with the polyol sodium salt (see Section 4) in molten polyol. Mannitol was the preferred polyol

$$RSO_2Cl + NaO\text{-}R'\text{-}(OH)_x \longrightarrow RSO_3R'\text{-}(OH)_x + NaCl$$

because of its lower melting point. (This method was used in the preparation of resin polyol ethers and is discussed in more detail below.)

As calculated from weight gain, the yields in Runs 202 and 204 were still low. However, these yields are misleading in that the weight gain due to esterification was offset by weight loss caused by the high reaction temperatures. The evolution of acid (and a consequent loss in

$$2RSO_3H \longrightarrow H_2SO_4 + RSO_2R$$

weight) was indicated by the neutralization of the excess sodium salt, as well as by a darkening in color which heating in sulfuric acid produces.

The sulfur and chlorine contents of Run 194 (Table 8) — which was prepared similarly to 202 — were consistent with a 52% yield of ester (and 48% residual sulfonate), considerably greater than Run 202's 12% yield based on weight gain. Similarly, the elemental analyses for the product in Run 204 corresponded to a 45% yield of ester (and 55% residual sodium sulfonate), which was also considerably larger than the weight-gain yield.

TABLE 7

PREPARATION OF RESIN POLYOL SULFONATES

Run	Sulfonyl Chloride, g	Polyol, g	Medium, ml	Base	Temp, °C	Time, hr	Yield, %(a)
77-SP	D50W, 4.3	Pyrogallol. 3.8	DMF, 45	Pyridine, 2 ml	75-80	4.5	58.0
77-SM	D50W, 2.5	Mannitol, 2.1	DMF, 20	Triethylamine, 5 ml	100	4	41.0
142-SM	ES-1, 3.0	Mannitol, 3.3	Dioxane/Water (10:1), 44	Triethylamine,	100	4	9.6
202-SS	ES-1, 3.0	Sorbitol, 25	MEE(b), 8; Toluene, 10	Sorbitol sodium salt, 4.6g(c)	130	16	11.6
204-SM	ES-1, 3.0	Mannitol, 25	MEEE(d), 8; Toluene, 10(c)	Mannitol sodium salt, 4.6g	180	16	14.4

(a) Expressed as percent of the theoretical weight gain.

(b) Bis(2-methoxyethyl) ether.

(c) Also 2.2g of sodium iodide.

(d) Bis [2(2-methoxyethoxy) ethyl] ether.

TABLE 8

ELEMENTAL ANALYSIS OF RESIN POLYOL SULFONATES

Sulfonate	Cl, %	N, %	S, %		
			Found	Calculated	
				RSO_2Cl	$RSO_3R'(OH)_x$
77-SP	0.5-0.8[a]	-	10.9	14.3	10.2
77-SM	2.0	4.6	10.7	13.5	8.4
142-SM	0.25	0.29	11.7	15.8	9.2
194-SS[b]	0.56	0.40	11.3	15.8	9.2
204-SM	0.80	0.08	11.8	15.8	9.2

(a) The range of chlorine values found in preparations similar to 77-SP.

(b) Prepared similarly to Run 202-SS (Table 7).

Resin Polyol Sulfonamide

The reaction of resin sulfonyl chlorides with N-methylglucamine (NMG) in DMF or wet dioxane media provided the polyol sulfonamides. Two equivalents of NMG were used, thereby eliminating the need for a second base to bind the acid produced.

$$RSO_2Cl + 2HN(CH_3)\text{-}R'\text{-}(OH)_2 \longrightarrow RSO_2N(CH_3)\text{-}R'\text{-}(OH)_x + NMG \cdot HCl$$

When the reaction was carried out in DMF, the product appeared to contain dimethylamine (from the degradation of DMF), present either as a sulfonamide or a sulfonate salt. Reaction in wet dioxane provided higher yields and a product from which nitrogenous impurities were completely removed by washing with 2% HCl solution. The order of increased yields observed in Runs 97, 105, and 126 of Table 9 parallels the increase in sulfonyl chloride reactivity (or porosity) in going from the conventional D50W derivative to the more porous, macroreticular A200 derivative to the still more porous ES-1 derivative. The sulfonamides' nitrogen contents corresponded well with the yields obtained.

Resin Polyol Carboxamide

Polyol carboxylic amides were prepared by the reaction of the carbonyl chloride/anhydride intermediate with NMG in DMF medium.

$$RC(O)Cl + (RCO)_2O + 3\ HN(CH_3)\text{-}R'\text{-}(OH)_x \longrightarrow$$
$$RC(OH)N(CH_3)\text{-}R'\text{-}(OH)_x + RCOOH + NMG \cdot HCl$$

Unlike the results experienced with the resin sulfonyl chloride, DMF was a satisfactory reaction medium, undergoing little or no decomposition. Typical procedures are summarized in Runs 66 and 86 (Table 9). The nitrogen contents of the products were in satisfactory agreement with the yields calculated on the basis of weight gain.

Resin Polyol Ethers

The first route investigated, the base-catalyzed reaction of the ES-1 chloromethyl derivative with polyols, was unsatisfactory when attempted

$$RCH_2Cl + R'OH \xrightarrow{base} RCH_2OR' + HCl$$

with either sodium hydroxide or organic amines, such as pyridine, triethylamine or dimethylaniline. The former was insufficiently reactive; the latter competed with the polyol for the chloromethyl compound, forming an organic ammonium chloride (a typical anion exchanger composition).

TABLE 9

PREPARATION OF RESIN POLYOL AMIDES

Run	Acid Chloride, g	NMG, g	Medium, ml	Temp., °C	Time, hr	Yield, %(a)	Cl, %	N, %	
								Found	Theory(b)
97-SN2	D50W, 2.5(c)	4.5	D/W(d), 25	100	3	35.0	0.74	1.09	3.54
105-SN1	A200, 5.0(c)	8.5	D/W, 44	100	3	47.2	1.07	2.28	3.40
126-SN	ES-1, 20(c)	4.3	D/W, 22	100	1.5(e)	71.0	0.66	2.84	3.79
66-AN	IRC-50, 1.2(f)	3.2	DMF, 30	85-90	4	53.0	(g)	3.38	5.22
86-AN	IRC-50, 3.0(f)	9.0	DMF, 40	90-105	10	59.2	(g)	3.92	5.22

(a) Expressed as percent of theoretical weight gain.

(b) For a 100%-converted N-methylglucamide.

(c) Resin sulfonyl chloride.

(d) Dioxane/water (10:1, vol).

(e) Longer reaction times (3 to 5 hours) gave similar results.

(f) Resin carbonyl chloride/anhydride

(g) Qualitative tests for chlorine were negative.

$$RCH_2Cl + Z_3N \longrightarrow RCH_2NZ_3Cl$$

In the second approach, the quatenary ammonium and dimethylsulfonium chloride derivatives of the ES-1 copolymer were condensed with polyols at relatively high temperatures in the presence of caustic (Reference 16).

$$RNMe_3Cl + HO\text{-}R'\text{-}(OH)_x \xrightarrow{NaOH} RO\text{-}R'\text{-}(OH)_x + Me_3N + NaCl + H_2O$$

$$RSMe_2Cl - HO\text{-}R'\text{-}(OH)_x \xrightarrow{NaOH} RO\text{-}R'\text{-}(OH)_x + Me_2S + NaCl + H_2O$$

The product from the ammonium chloride reaction showed no increase in weight; 90% of the beads were shattered and the remainder were reduced to a fine powder. Although the infrared spectrum contained strong hydroxyl and ether absorptions, the chlorine and nitrogen contents were consonant with a residual trimethylammonium content of 30% (22% as hydroxide and 8% as chloride).

An incompletely reacted product was also obtained from the sulfonium halide attempt. Although the product again exhibited an ether absorption in the infrared, there was a loss in weight, and the sulfur analysis indicated a 37% content of residual resin dimethylsulfonium hydroxide. The prime objection to both products, of course, was that their significant residual anionic contents would result in misleading and overly large phosphorus capacity when the products were tested.

The resin polyol ethers were prepared in satisfactory purity and good yield, however, when the ES-1 chloromethyl derivative was reacted with the sodium salt of a polyol in molten polyol medium (Table 10). Sodium iodide was added to increase the reactivity of the chloromethyl compound through halogen exchange (Reference 17), and small amounts of high-boiling ethers served to swell the resin and make the mixtures more fluid. Both the iodide and the ether were necessary for good conversion; when either was absent, the reaction proceeded to only a small extent. Toluene effected the azeotropic removal of water, with considerable improvement in yield (compare Runs 198 and 203).

The products exhibited strong ether absorption in the infrared (1040-1100 cm^{-1}). The higher yield obtained with sorbitol (Runs 203 and 200) is perhaps due to the lower reaction temperature made possible by the lower melting point of sorbitol. In order to see if the ether was being retained by the beads and thus contributing to the gain in weight observed, Runs 200 and 203 were repeated but without the sodium iodide and the polyol salt; there was no gain in weight, indicating that the ether was not being retained.

Just as in the preparations made from the quaternary ammonium and dimethylsulfonium halides, the yields noted in Table 10 are spuriously low because of the degradation-caused weight losses that undoubtedly

TABLE 10

PREPARATION OF RESIN POLYOL ETHERS

Run	Chloromethyl ES-1, g	Polyol Sodium Salt, g	Sodium Iodide, g	Polyol, g[a]	Ether, ml	Toluene, ml	Temp, °C	Time, hr	Yield, %[b]
198-CS	3.5	S, 6.1	3.6	S, 25	5[c]	-	160	16	17.1[d]
200-CM	3.3	M, 6.5	4.1	M, 25	8[e]	10	190	16	28.7[f]
203-CS	3.3	S, 6.5	4.1	S, 25	8[c]	10	130	16	41.3

(a) M, mannitol; S, sorbitol.

(b) Expressed as percent of theoretical weight gain.

(c) Bis(2-methoxyethyl)ether.

(d) Analysis: 3.8% Cl and 0.23% N. (Equivalent to a polyol ether containing 27% RCH_2Cl and 1% RCH_2NH_3OH).

(e) Bis [2(2-methoxyethoxy)ethyl] ether.

(f) Analysis: 2.07% Cl and 0.21% N. (Equivalent to a polyol ether containing 16% RCH_2Cl and 1% RCH_2NH_3OH).

occurred. This belief is supported by the chlorine analyses, which correspond to residual chloromethyl resin contents of 27% for Run 198 and 16% for Run 200. In both products the nitrogen content was insignificant.

Silanol Resins

The preparation of silanol resins was limited to a single attempt at each of the following reactions:

$$RCH_2Cl + H_2N(CH_2)_3Si(OEt)_3 \longrightarrow \xrightarrow{H_2O} RCH_2NH(CH_2)_3Si(OH)_3$$

$$RSO_2Cl + H_2N(CH_2)_3Si(OEt)_3 \longrightarrow \xrightarrow{H_2O} RSO_2NH(CH_2)_3Si(OH)_3$$

Overnight stirring of ES-1 chloromethyl resin with excess γ-aminopropyl-triethoxysilane at 90° provided (after thorough washing with water, rinsing with acetone, and drying) a 51% yield of the aminosilanol (putative). A similar treatment of the sulfonyl chloride at 75° for four hours gave only a 10% yield of the sulfonamide (putative).

Resin/Metal Sorbents

A brief investigation of resin/metal sorbents for phosphate removal was conducted during the latter part of the initial 12-months program. Promising results were obtained with sorbents prepared from cation exchangers (Na form) and aqueous solutions of iron or aluminum chloride. Based on these results, a 6-months extension was granted to study phosphate removal by resin/metal sorbents.

In aqueous solution, these metallic cations are hydrated and behave as acids in the Bronsted sense by donating protons to the solvent water molecules. Thus, the hydrated iron (III) ion hydrolyzes acidically as follows:

$$Fe(H_2O)_6{}^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+$$

$$Fe(H_2O)_5(OH)^{2+} + H_2O \rightleftharpoons Fe(H_2O)_4(OH)_2{}^+ + H_3O^+$$

These products are also believed to be capable of further reaction to produce higher molecular weight (and correspondingly less soluble) polymers (Reference 18).

Between pH 2 and 3, the major species present in iron solutions at a total iron concentration of 1×10^{-3} M are $Fe(H_2O)_6{}^{3+}$ and $Fe(H_2O)_5(OH)^{2+}$ (Reference 18). Assuming a similar situation holds in more concentrated solutions, the reaction between the cation exchanger and aqueous ferric chloride solution involves mainly the following reactions (water of hydration is neglected for simplicity).

$$3\ RSO_3^- + Fe^{3+} \longrightarrow (RSO_3^-)_3Fe^{3+}$$

$$2\ RSO_3^- + FeOH^{2+} \longrightarrow (RSO_3^-)_2Fe(OH)^{2+}$$

Presumably the aluminum salt reaction follows a similar course, although the hydrolysis of aluminum is believed to be more complicated than that of iron (Reference 19).

When 5 g (22.2 meq) of A200(Na) was stirred with 12 g (44.4 mmoles) of ferric chloride in one liter of water, the vacuum-dried product contained 10.0% Fe, or 1.79 mmoles Fe/g of product. Assuming all the sodium ions were replaced by iron, each gram of product contains 0.900/0.2022 or 4.46 meq of resin (where RSO_3^- has an equivalent weight of 202.2).

Let x = meq of Fe^{3+} on resin

y = meq of $FeOH^{2+}$ on resin

then, $x + y = 1.79$ (1)

$3x + 2y = 4.46$ (2)

multiplying (1) by (2) and subtracting

$$\begin{aligned} 3x + 2y &= 4.46 \\ \underline{2x + 2y} &= \underline{3.58} \\ x &= 0.88 \\ y &= 0.91 \end{aligned}$$

The product, if the assumption is valid (which appears reasonable), contained approximately equal amounts of Fe^{3+} and $FeOH^{2+}$ ions. Lacking data on the ease of removal of hydrate water from sorbed iron, it does not appear possible to determine with certainty the nature of the sorbed iron. The presence of large amounts of $Fe(OH)_2^+$ appears unlikely, however, since this would leave 2.67 meq (vide supra) of Na^+ on a resin which has been treated with a two-fold excess of Fe^{3+}.

The preparation of resin/metal sorbents has been accomplished by three different procedures. In the Batch Process (above), the resin was stirred for several hours with a solution of a multivalent metal salt. In early experiments the product was washed with water and acetone and vacuum dried. It was found, however, that the measured weight gains did not correlate with phosphorus capacity. Furthermore, higher capacities were obtained with samples of resin/iron sorbents which had not been dried after preparation, and the practice of drying the resin/metal sorbents was discontinued.

A second method of preparation, the Drip Process, was used in early experiments comparing various resin/metal sorbents, which consisted of dropping the ferric chloride solution onto the resin in the same manner as used in evaluating Procedure 1 (*vide infra*). After the sorbent was washed with water on the filter, the phosphorus capacity was determined by Procedure 1.

The third, and most successful, method for preparing resin/metal sorbents was the Column Process. A column of resin was prepared in water and classified by backwashing. The ferric chloride was added at a flow rate determined by the diameter of the column; e.g., 0.25 ml/min, 2.1 ml/min, and 3.0 ml/min for 0.9-cm, 2.5-cm, and 3.0-cm columns, respectively. The sorbent was washed thoroughly with water, reclassified if air bubbles had developed, and exhausted in the same column. The liquid level was maintained above the resin column at all times. This latter procedure provided sorbents of consistently higher capacity than those prepared by the other procedures, and proved to be the method of choice (*vide infra*).

SORBENT EVALUATION

Evaluation of the phosphorus capacities of the various sorbents required, initially, rapid screening procedures to compare the relative capacities of different samples. For optimization of the phosphate removal process, however, more accurate results were necessary to evaluate the effects of various changes in the processes involved in sorbent preparation, exhaustion, and regeneration. To fill these differing needs three procedures were utilized.

For optimum utilization of resin capacity, a minimum bed depth of 24 in. is recommended (Reference 20). In wide resin beds, flow rates of 2 gal/min-ft^3 of resin are readily achieved (this is equivalent to 0.27 ml/min-ml of resin). For the present program, a bed depth of 24 in. presented two disadvantages. A 2.5-cm I.D. column 60 cm (24 in.) deep would require nearly 300 ml of resin, while even a 1.0-cm column would need 38 ml of resin to achieve that bed depth. Furthermore, the flow rates needed for satisfactory phosphate removal were found to be drastically reduced in narrow columns. In 0.9 to 1.0-cm columns, 6.5 cm deep, a flow rate of 0.25 ml/min was necessary for satisfactory performance. At this flow rate a 24-in. deep bed would require over 300 hours to exhaust, if the solution contained 8 mg P/l. and the phosphorus capacity was 1 mg/ml (a low value). Rather than use unrealistically high phosphorus concentrations to provide reasonable exhaustion times, resins were evaluated under non-optimum conditions. Rapid comparisons between different sorbents were made using a wide, shallow bed

(Test Procedures 1 and 2), while a deeper, narrower bed (0.9 x 6.5 cm) was used for obtaining more critical data during optimization runs (Test Procedure 3). In Test Procedure 1 the test solution (generally 8.16 mg P/l. and 500 mg NaCl/l.) was added at a rate of 1.4 ± 0.1 ml/min. Effluent was collected in 50-ml increments until the arbitrary breakthrough of 0.326 mg P/l. (equivalent to 1 mg/l. of PO_4) was reached. As applied to XE-243, a 2-g (dry wt) sample was taken; with the resin/metal sorbents, a 1-g (dry wt) sample was used.

In Test Procedure 2, the test solution was added to 2 g (dry wt) of sorbent at a rate of 1.0 ± 0.1 ml/min. Three 25 ml increments of effluent were collected and analyzed for phosphorus content. This procedure was used on the polyol resins, which had a relatively low capacity. Usually, the sample's capacity was exhausted after the second increment was collected.

In Test Procedure 3, a sample of 4.6 ml of sorbent was exhausted in a classified (backwashed) 0.9 x 6.5-cm bed in a 25- or 50-ml buret. The solution was added at a rate of 0.25 ml/min. The acquisition of data was accelerated by the finding that raising the phosphorus concentration from 8 to 25 mg P/l. had negligible effect on the phosphorus capacity or leakage. As expected, the phosphorus capacities were higher, the leakage lower, and the data more precise with the more time-consuming Test Procedure 3 than with Test Procedure 1.

Test Procedures 1 and 2 were used for initial evaluation of sorbent preparation and regeneration procedures, taking care to make comparisons only between sorbent data obtained by the same procedure.

Capacity evaluations were also performed with other test solutions, including a polyphosphate solution and natural secondary effluents. These results are discussed below.

XE-243

In order to verify Test Procedure 1 and to have a firm basis for comparison with other sorbents, a number of capacity evaluations were performed on XE-243. As shown in Table 11, highly reproducible data were obtained. In two regeneration experiments (Runs 37 and 44), the sorbed phosphorus was readily removed by 5% sulfuric acid solution.

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In Test Procedure 2, the test solution was added to 2 g (dry wt) of sorbent at a rate of 1.0 ± 0.1 ml/min. Three 25 ml increments of effluent were collected and analyzed for phosphorus content. This procedure was used on the polyol resins, which had a relatively low capacity. Usually, the sample's capacity was exhausted after the second increment was collected.

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TABLE 11

PHOSPHORUS CAPACITY OF XE-243

Run	P Removal, mg	Breakthrough Concentration, mg P/l	P Capacity, mg/ml wet resin
37[a]	1.91	0.391	0.281
38	1.90	0.456	0.279
44[a]	1.91	0.652	0.281
45	1.90	0.564	0.279
48	1.94	0.251	0.285
49	1.93	0.440	0.284

[a] Regeneration with 100 ml of 5% H_2SO_4 solution removed 1.87 mg P in Run 37 and 1.95 mg P in Run 44. In each case, the difference between P sorbed and P recovered was within the 2% accuracy of the assay.

The phosphorus capacities of XE-243 for polyphosphate and dihydrogenphosphate ($H_2PO_4^-$) ions were also determined. Test Procedure 1 was followed, except that the source of phosphorus was different. The polyphosphate effluent solutions were boiled for 40 minutes before analysis in order to depolymerize the phosphate species to the orthophosphate form. As can be seen in Table 12, the capacities for $H_2PO_4^-$ and polyphosphate were approximately 50 and 100% greater than the capacity for HPO_4^{2-} (Table 11). Both species were strongly sorbed by the resin; removal of these phosphates required larger amounts of sulfuric acid than was needed for HPO_4^{2-}. A possible mechanism for the sorption of orthophosphate ions by polyols is described in the Appendix.

Resin Polyol Amides and Esters

The polyol resins initially synthesized in the program were sulfonamide and sulfonate ester derivatives of D50W and the carboxamide derivative of IRC-50. Although the IRC-50 product had a somewhat higher capacity than the other resins, all the retentions were quite low, being at best no more than 7% of that of XE-243 (Table 13).

Several possible explanations were considered. First, the relative extent of conversion of the chloromethyl precursor to the polyol derivative was estimated at 67% (based on the 3.74% N content of XE-243) in the case of XE-243, or only slightly more than the 50 to 60% conversions

TABLE 12

CAPACITY OF XE-243 FOR DIHYDROGENPHOSPHATE AND POLYPHOSPHATE

Run	Phosphate Species	P Removal, mg	Breakthrough Concentration mg P/l.	P Capacity, mg/ml wet resin	P Recovery by Regeneration, mg	Regenerant, ml	
						5% H_2SO_4	10% H_2SO_4
23	$H_2PO_4^-$ [(a)]	3.15	0.365	0.463	3.20	200	-
25	$H_2PO_4^-$	3.03	0.620	0.445	2.91	150	-
27	Polyphosphate[(b)]	3.95	0.358	0.580	3.98	600	250
28	Polyphosphate	3.98	0.277	0.585	4.02	-	500

(a) From sodium dihydrogenphosphate.

(b) From "sodium hexametaphosphate" (66.8-68.0% P_2O_5).

TABLE 13

PHOSPHORUS CAPACITY OF POLYOL RESINS

Run	Resin	Resin Type	Retained P, mg/2g dry resin	P Capacity, mg/ml wet resin
59	77-SP	D50W Pyrogallyl ester	0.011	0.0027
81	77-SM	D50W Mannityl ester	0.023	0.0046
87-2	87-SN	D50W N-methylglucamide	0.024	0.0050
66	86-AN	IRC-50 N-methylglucamide	0.043	0.0056
133	XE-243	SDVB N-methylglucamide	0.591	0.0870

of resin sulfonyl chloride or resin carbonyl chloride to the analogous amide and ester derivatives (see Tables 7 and 9). These small differences in polyol content were not a likely cause for the relatively large capacity difference observed.

A second possibility was that passage of the test solution through the polyol products (which are normally washed with acid during workup) would promote exchange of H^+ for Na^+ at the residual SO_3H functions, and to a lesser degree at the residual COOH groups in the IRC-50 products. The resulting acidity would tend to counteract phosphorus uptake. A first test of this hypothesis was made by determining the phosphorus capacity of two polyol products after a prior treatment with dilute NaOH solution to convert residual sulfonic acid to the sodium salt. As shown in Runs 74 and 87-3 of Table 16, there was some improvement for the D50W resin and essentially no change for the IRC-50 product (see Runs 87-2 and 66, Table 13).

In a second test of this hypothesis a batch of the D50W N-methylglucamide resin was prepared in the usual way except that the work-up procedure was modified so as to preclude the transformation of unreacted sulfonyl chloride to sulfonic acid. (Instead of wash treatments with water and dilute hydrochloric acid solutions, the product was rinsed with DMF and acetone, and then dried.) Portions of this material were reacted (separately) with 10% ammonia solution and with di-n-propylamine. Elemental analysis of the products yielded N contents of 5.38% and 4.98%, respectively, indicating that large amounts of base had been introduced as amide or salt. (The theoretical value for a fully converted D50W N-methylglucamide is 3.54% N.)

Comparison of Runs 87-5 and 87-6 (Table 14) with Run 87-2 (Table 13) shows the phosphorus capacity had increased, but was still much less than that of XE-243. In the case of the IRC-50 product, the probable explanation for the failure of basic treatment (Run 74) to improve the capacity (see Run 66, Table 13) is that the residual COOH content, because of its slightly ionized nature, had done little to inhibit phosphorus uptake in the first place. It is considered significant that the sample of highest capacity (Run 87-5) underwent no swelling in water, whereas the other materials showed volume increases of 60 to 70%. This is explained on the basis that swelling is essentially due to the solvation of residual SO_3H, and too few of such functions remained in 87-5 after the reaction with the amine. The conclusions from these experiments were that residual SO_3H did have a capacity-lowering effect and that basic conditioning of the polyol resins before evaluation was desirable, but that the conditioning treatment per se could not increase the capacity of these resins to a satisfactory level.

A third possibility was that the low phosphate uptake was due to an insufficient swelling of the resin in water, with a consequent inadequate access of phosphate to the polyol portion. To test this hypothesis, the relative swelling in water of three polyol resins, four sulfonic acid

TABLE 14

PHOSPHORUS CAPACITY OF BASE-TREATED POLYOL RESINS

Run	Resin	N-Methylglucamide	Treatment	Retained P, mg/2g dry resin	P Capacity, mg/ml wet resin
74	86-AN	IRC-50	2% NaOH[a]	0.041	0.0054
87-3	87-SN	D50W	2% NaOH[b]	0.039	0.0081
87-5	87-SN	D50W	Di-n-propylamine[c]	0.028	0.0093
87-6	87-SN	D50W	10% ammonia[d]	0.036	0.0075

[a] Dropwise addition of 25 ml of 2% NaOH solution, followed by 20 ml of water.

[b] Stirring for one hour, followed by washing with water.

[c] Stirring overnight, followed by washing with acetone.

[d] Stirring overnight, followed by washing with water.

cation exchangers, two weak-acid cation exchangers, and XE-243 was measured. As shown in Table 15, the degree of swelling of the polyol resins was greater than that of XE-243, particularly for the two resins (62 and 86) which, like XE-243, are N-methylglucamine derivatives. Obviously, the low phosphate sorption of these products cannot be attributed to a mere lack of swelling.

A particularly interesting aspect of this data, however, was the relatively low density (or high porosity) of XE-243, compared with the other resins, as indicated by the respective volumes of 1-g samples. This suggested a fourth possibility - that the low phosphate capacity of the polyol resins was due to a relatively dense or nonporous nature. This assumption was supported by the fact that XE-243 has a nominal DVB content of only 1% (Reference 21), whereas the DVB content of D50W is 8%.

In order to study the relationship of resin density to phosphorus capacity, the preparation of low density or relatively porous sorbents was undertaken beginning with (1) A200, a commercially available, macroreticular sulfonic acid exchanger, and (2) ES-1, an Aerojet-synthesized, 1%-crosslinked SDVB copolymer. Macroreticular resins have been variously described as having pore sizes from one to several orders of magnitude greater than that of the conventional gel-type resins (Reference 22). The 1%-crosslinked copolymer was expected to be less dense than the materials previously used, and possibly more reactive. With both resins, the usual synthetic approach through the sulfonyl chloride intermediate was taken.

The phosphorus capacities of the resulting polyol resins are given in the first four rows of Table 16. The macroreticular polyol resin (105) showed much the same capacity as the conventional D50W and IRC-50 polyols previously tested (Table 13). Apparently, the macroreticular structure with its larger pores did little to enhance phosphorus retention. In the case of the ES-1 ester and amide resins, however, a much larger increase in capacity resulted, relative to the higher-crosslinked D50W resins. Although a portion of this improvement can be attributed to the higher yields obtained in the esterification of the ES-1 sulfonyl chloride relative to its D50W analogs (Table 9), the major improvement was probably due to an increased porosity. Nevertheless, the capacities of the ES-1 polyols were still less than 20% of the value for XE-243 (Table 13).

Resin Polyol Ethers

Because of the general desirability of increased porosity and elimination of residual acidic functions in the polyol sorbents, the resin polyol ethers were attractive for investigation. These materials would contain no residual acidic groups as a result of incomplete conversion during their synthesis and, as ethers, would be inherently more stable to hydrolysis than the ester or amide derivatives. In addition, they could be prepared in low-crosslinked form, beginning with the ES-1 chloromethyl derivative.

TABLE 15

SWELLING OF VARIOUS RESINS IN WATER(a)

Resin	Chemical Nature	Volume, ml(b)	Volume Increase, %
62-SN	D50W N-methylglucamide	1.3	69
77-SP	D50W Pyrogallyl ester	1.4	43
86-AN	IRC-50 N-methylglucamide	1.9	100
IR-118	SDVB Sulfonic acid, < 5% DVB	1.3	161
IR-120	SDVB Sulfonic acid, 8% DVB	1.5	80
IR-124	SDVB Sulfonic acid, 12% DVB	1.3	69
A200	SDVB Sulfonic acid, 20% DVB(c)	1.8	56
IRC-50	Methacrylic-DVB copolymer(d)	1.7	65
IRC-84	Acrylic acid copolymer(e)	1.4	50
XE-243	SDVB N-methylglucamide	2.6	38

(a) Procedure: 3.5 ml of water was added to 1 g of dry resin in a calibrated vial and the resin's increase in volume after standing overnight was noted.

(b) The volume occupied by 1 g of dry resin.

(c) Macroreticular.

(d) Nominal DVB content is not known.

(e) Nature and amount of crosslinking is not known.

TABLE 16

PHOSPHORUS CAPACITY OF HIGH-POROSITY POLYOL RESINS[(a)]

Run	Resin	Resin Type	Retained P, mg/2g dry resin	P Capacity, mg/ml wet resin
112	105-SN2	A200 N-methylglucamide	0.031	0.0071
138	127-SN	ES-1 N-methylglucamide	0.081	0.010
204	204-SM	ES-1 Mannityl Sulfonate	0.121	0.014
194	194-SS	ES-1 Sorbityl Sulfonate	0.129	0.014
200	200-CM	ES-1 Mannityl Ether	0.045	0.012
203	203-CS	ES-1 Sorbityl Ether	0.044	0.012

(a) Prior to capacity evaluation, the resins were washed with dilute NaOH solution.

The phosphorus capacity data for ES-1 polyol ethers is shown in Table 16 (Runs 200 and 203). On the dry basis, the phosphorus retentions were considerably lower than those obtained with the analogous polyol esters and amide (138, 204, 194). Possibly, intermolecular ether formation at the high synthesis temperatures employed (Table 10) decreased the number of available hydroxyl groups. On the wet-basis, the capacities were essentially the same as that of the esters and amides because the ethers underwent only 12% swelling in water instead of the 38 to 100% noted with the other derivatives (Table 15). The low degree of swelling was probably due to the absence of highly solvatable acid functions (such as SO_3H) and to the hydrophobic ether function.

Silanol Resins

As noted in the Sorbent Synthesis discussion, the limited effort expended in the preparation of silanol resins provided an aminosilanol (51% conversion) and a sulfonamide (10% conversion). The phosphorus capacity of the amine, as determined by Test Procedure 1, was comparable to that of the polyol resins; the capacity of the amide was negligible, as might be expected from the poor conversion obtained.

Resin/Metal Sorbents

Compared to the polyol resins, resin/metal sorbents, prepared by conversion of cation exchange resins to their iron (III) or aluminum forms, had very high phosphorus capacities. Table 17 shows phosphorus capacity data (determined by Test Procedure 1) for sorbents prepared from IRC-50 (a weak acid cation exchanger), ES-1S, and A-200 (strong acid exchangers) by reaction with ferric or aluminum chloride. For comparison purposes, the quaternary (strong base) anion exchange resin IRA-400 is included. It can be seen from Table 17 that, on a weight basis, five of the sorbents had phosphorus capacities greater than that of XE-243, while three sorbents exceeded the capacity of the anion exchanger, IRA-400. For all three cation exchange resins (IRC-50, ES-1S, and A-200) the iron form had significantly higher capacity than the aluminum form.

It is likely that the lower capacity of the ES-1S product in Run 237 was due more to the greater swelling this low-crosslinked resin underwent in water than to an intrinsically lesser capacity for phosphate. In Run 243, the evaluation could not be completed because the flow rate slowed near the end of the determination; when the test was stopped, the resin had already taken up as much phosphorus as had Run 242. Larger sorbent beads would probably provide better results.

The greater phosphorus capacities of the A200 sorbents as compared to the IRC-50 resins, and the commercial availability of the Amberlite 200 resin (as compared to ES-1S), suggested that our efforts should be concentrated on the development of A200/metal sorbents, of which the iron

TABLE 17

PHOSPHORUS CAPACITY OF RESIN/METAL SORBENTS[a]

Run	Sorbent	Wet Volume,[b] ml	P Removal, mg	Breakthrough Concentration mgP/1.	P Capacity, mg/ml wet resin
227	IRC-50/Al	3.1	0.763	0.440	0.12
228	IRC-50/Fe	2.7	1.161	0.326	0.22
237	ES-1S/Al	4.1	4.689	0.339	0.57
243	ES-1S/Fe	4.2	> 7.4[c]	-	-
235	A200/Al	2.6	5.831	0.339	1.12
242	A200/Fe	2.3	7.409	0.375	1.61
146	IRA-400[d]	3.6	4.679	0.391	0.65
37	XE-243	3.4	1.914	0.391	0.28

[a] Capacity was determined on a 2-g sorbent sample.

[b] Volume occupied by 1g of dry resin after overnight immersion in water.

[c] The evaluation could not be completed because the flow rate decreased near the end of the determination.

[d] A quaternary ammonium anion exchanger.

(III) form appeared to be most suitable. Several A200/Fe sorbents were prepared, evaluated by Test Procedure 1, and subjected to regeneration.

Because the time required to obtain the capacity data in Table 17 proved excessive (11 hours), the size of resin sample was reduced from 2 to 1 g for subsequent evaluation, all other test parameters being left unchanged. Using this revised procedure, the data summarized in Table 18 was obtained on A200-Fe sorbents. It is of interest to note the disproportionate effect that halving the sorbent sample size had on the observed phosphorus capacity. Thus, the 1-g sample of A200-Fe sorbent (Run 251, Table 18) retained only 21.4% as much P as did the 2-g sample (Run 242, Table 17). This behavior was perhaps due to the increased channeling that may result in the smaller sorbent sample (shollower resin bed).

The identical capacity values obtained in Runs 249 and 251 indicated that the form (H or Na) in which the resin is utilized is unimportant. Sorbents prepared by the Drip Process and evaluated without prior drying (Runs 274 and 271 (A-F) had an average capacity value (0.91 mg/ml wet resin) that was about 34% higher than sorbents obtained by stirring the exchanger in $FeCl_3$ solution and then drying the product (0.68 mg/ml wet resin). Although drying may reduce the capacity, later experiments (vide infra) showed that the Drip Process is more effective than the batch method of preparation.

In addition to the iron sorbents prepared from A200, a number of other multivalent metal ions were tested as A200 derivatives for phosphorus sorption capacity. A summary of these experiments is shown in Table 19. It is apparent from the table that, of the ions tested, Fe (III) is by far the most effective for sorption of phosphorus on a cation exchange resin.

As the superiority of the phosphorus capacity of A200-Fe over other resin metal sorbents became increasingly evident, a study of the conditions of its preparation was initiated. To provide greater sensitivity to changes in phosphorus capacity, Test Procedure 3 (vide supra) was adopted. For evaluation of process changes, resin samples of 4.6 ml (wet volume) were tested in 0.9 to 1.0-cm columns, giving a bed depth of approximately 7 cm. A brief study of flow rates showed that satisfactory phosphorus removal was accomplished at a flow rate of 0.25 ml/min. Samples of A200-Fe were prepared by the Batch, Drip, and Column Processes (vide supra) and evaluated by Test Procedure 1 and Test Procedure 3. The results, shown in Table 20, show the increased efficiency of Test Procedure 3, which undoubtedly results from reduced channeling and improved equilibration between sorbent and solution. It is also apparent that, while the Drip and Column Processes produced sorbents with equivalent phosphorus capacities, the capacity of the Batch-prepared sorbent was definitely inferior. Since the Column Process appeared (visually) to afford better contact between resins

TABLE 18

PHOSPHORUS CAPACITY OF A200-Fe SORBENTS(a)

Run	Sorbent	P Removal, mg	Breakthrough Concentration, mg P/l.	P Capacity, mg/ml wet resin
249	249(b)	1.571	0.434	0.68
251	245(c)	1.581	0.326	0.69
271A(d)	249	2.794	0.381	1.22
271B	249	2.403	0.368	1.04
271C	249	1.963	0.489	0.85
271D	249	1.992	0.349	0.87
271E	249	1.575	0.342	0.68
271F	249	1.999	0.346	0.87
271G	249	1.998	0.326	0.87
271H	249	1.554	0.567	0.67
271 I	249	1.989	0.385	0.86
274	274(e)	1.994	0.375	0.87

(a) Capacity was determined on a 1-g sorbent sample by Test Procedure 1.

(b) Prepared from the H form by the Batch Process.

(c) Prepared from the Na form by the Batch Process.

(d) In Runs 271 (A-I) one resin sample was regenerated nine times by the Drip Process.

(e) Prepared by the Drip Process and evaluated without prior drying.

TABLE 19

PHOSPHORUS CAPACITIES OF SORBENTS PREPARED FROM A200 AND VARIOUS MULTIVALENT METAL IONS(a)

Run	Sorbent	Source of Metal Ion	Total P Sorbed, mg	Breakthrough Concentration, mg P/l.	P Capacity, mg/ml wet resin
263A	A200/Al	$AlCl_3$	1.13	0.49	0.49
263B	A200/Al(b)	$AlCl_3$	1.59	0.38	0.69
372	A200/Al	$Al(OAc)_2OH$	--	0.60	nil
376	A200/Al	$Al(OAc)_2OH$	0.39	0.32	0.17
282	A200/Ca	$CaCl_2$	--	--	nil
384	A200/Ca	$CaCl_2$	--	--	nil
371	A200/Fe	$FeCl_3$(c)	1.19	0.31	0.52
382A	A200/Fe	$FeCl_3$(d)	2.39	0.34	1.04
355	A200/La	$LaCl_3$	--	--	nil
385	A200/Mg	$MgCl_2$	--	--	nil
264	A200/Zr	$ZrCl_4$	0.38	0.62	0.16
265	A200/Zr	$ZrOCl_2$	0.38	0.68	0.16

(a) P Capacity determined on 2.3-ml samples by Test Procedure 1.

(b) Sorbent 263A regenerated with $AlCl_3$.

(c) 1480 ml of 0.001 M $FeCl_3$, pH 2.0 (adjusted with concentrated HCl).

(d) 100 ml of 0.1 M $FeCl_3$, pH 3.0.

TABLE 20

EFFECT OF METHOD OF PREPARATION ON PHOSPHORUS CAPACITY OF A200-Fe SORBENTS

Run	Sorbent[(a)]	Preparation Process	P Capacity Test Procedure	P Capacity, mg/ml wet resin
407A	407A	Batch	1[(b)]	0.52
407B	407B	Drip	1[(b)]	0.34
407C	207C	Column	1[(b)]	0.34
408A	407A	Batch	3[(c)]	1.30
408B	407B	Drip	3[(c)]	3.09
408C	407C	Column	3[(c)]	2.83

(a) Sorbents were prepared in 46-ml lots.

(b) Determined on 2.3-ml samples.

(c) Determined on 4.6-ml samples.

and solution than did the Drip Process, sorbents for subsequent runs were prepared and regenerated by the former.

When the sorbents were prepared or regenerated by the Column Process in 4.6-ml lots, still higher capacities resulted. The results listed in Table 21 show the effects of varying the amount and concentration of ferric chloride on phosphorus capacity. In Runs 414 and 416, the results show no difference in capacity between sorbents prepared with 0.2M, 0.4M, and 1.0M ferric chloride solutions, where the amount of ferric chloride was held constant. In Run 421, the ferric chloride concentration was held constant while varying the amount of ferric chloride. The results indicated that reducing the amount of ferric chloride from 60 meq to 20 meq (per 4.6 ml of wet resin) decreased the phosphorus capacity by about 15%.

Because column-derived phosphorus capacity values are strongly dependent on the experimental conditions employed, it was of interest to measure the total capacity of A200-Fe sorbents. The resins were stirred overnight in phosphate solutions of known concentration, both in the presence and absence of added sodium chloride. Knowledge of the phosphorus content of the initial and final solutions provided the amount of phosphorus sorbed.

As is shown in Table 22, the (dry-basis) capacity varied from 7 to 52 mg/g sorbent, depending on the test solution employed. At very high phosphorus concentrations (Runs 254 and 286) the capacity was not affected by the presence of sodium chloride. At much lower and relatively realistic levels (Runs 267, 268, 259, and 260), sodium chloride appears to increase phosphorus capacity.

The regeneration of A200-Fe sorbents was accomplished by the dropwise addition (1.4 ml/min) of 150 ml of 5% sulfuric acid, 200 ml of 2.5% sulfuric acid, or 300 ml of 1% sulfuric acid solution. However, iron was also removed, as shown by (1) an 80% loss in phosphorus capacity on a subsequent exhaustion of the sorbent, and (2) by analysis of the iron content of the spent regenerant. (With the 1% sulfuric acid solution, 33% of the iron in the sorbent was removed during the phosphate stripping and 21% was removed with the first 50 ml of acid.) Basic regeneration was not attempted because preliminary experiments had shown that treatment of the sorbents with 2% ammonia solution greatly reduced their capacity.

Regeneration was completely successful, however, when performed by the dropwise addition of 50 to 200 ml of 0.1 M ferric chloride solution (pH 1). The spent regenerant was free of precipitate. A quantitative determination of the amount of phosphorus removed was not possible because of interference by the large amount of iron present. The evidence for a successful regeneration can be seen in Runs 249 and 271 (A-1) (Table 18), where a relatively constant phosphorus capacity was maintained over ten exhaustion/regeneration cycles with a single

TABLE 21

EVALUATION OF COLUMN-PREPARED A200/Fe SORBENTS BY TEST PROCEDURE 3[a]

Run	$FeCl_3$ Used, meq.	$FeCl_3$ Used, Concentration	P Capacity, mg/ml wet resin
414A	60	0.2 M	8.42[b]
414B	60	0.2 M	9.23[b]
416A	60	0.2 M	8.14[b]
416B	60	0.5 M	8.42[b]
416C	60	1.0 M	8.14[b]
421A	20	0.5 M	7.33
421B	40	0.5 M	6.24
421C	80	0.5 M	9.23

(a) 4.6-ml Lots of A200/Fe were prepared by the Column Process in 0.9 to 1.0-cm (ID) columns and evaluated in the same column by Test Procedure 3, using a solution containing 25 mg P/l.

(b) The average of these 5 runs is 8.47 ± 0.40 mg P/ml. If the high result of 414B is rejected, the average is 8.28 ± 0.14 mg P/ml.

TABLE 22

TOTAL PHOSPHORUS CAPACITY OF A200/Fe SORBENTS

Run	Sorbent Weight, g	Solution Volume, l	Initial Concentration		Final Concentration, mg P/l.	P Capacity	
			mg P/l.	mgNaCl/l.		mg/g dry resin	mg/ml wet resin
254	3	1	260	0	104.3	52.2	22.7
286	3	1	260	16,000	106.9	51.2	22.6
259(a)	1	2.5	32.6	0	29.80	6.9	3.0
260(a)	1	2.5	32.6	2,000	23.54	22.7	9.9
267	1	2.5	16.3	0	11.05	13.1	5.7
268	1	2.5	16.3	1,000	5.08	28.1	12.2

(a) These data are perhaps somewhat less reliable because the usual precautions of redrying the sorbent and rinsing glassware with hot HCl solution prior to testing were not observed.

sorbent sample. The small variations in observed capacity from cycle to cycle are probably due to unavoidable variations in the exhaustion cut-off (breakthrough) point and in the rate of solution addition.

In other early regeneration experiments, the use of weak acids and weak bases was studied, as well as the use of hydrochloric acid followed by ferric chloride treatment. The data in Table 23, obtained using Test Procedure 1, indicate that regeneration with ferric chloride, or hydrochloric acid/ferric chloride, is superior to the other regenerants. These two regenerant systems were investigated further using Test Procedure 3. When Batch-prepared A200-Fe was regenerated by the Column Process, phosphorus capacities equal to those found with Column-prepared A200/Fe sorbents (Table 24) were obtained. The data indicate that the added expense of hydrochloric acid treatment before regeneration with ferric chloride is not warranted.

Table 25 shows the results of a number of exhaustion/regeneration cycles with A200/Fe sorbents on secondary effluent from the Whittier Narrows Water Reclamation Plant. The amount of orthophosphate sorbed averages about 1.7 mg P/l. (Runs 412, 413, 415, 419, 420.) In Run 419, the total phosphorus capacity was found to be 2.75 mg P/ml. Phosphorus removal data for this run are shown in Table 26. Regeneration with ferric chloride was successful (Runs 413 and 415), but the amounts used were the same as for preparation, about 4 mmoles of ferric chloride per ml of resin (about 45 moles of Fe per mole of P). Treatment with sodium hydroxide, however, apparently produced a change in the sorbent that could not be reversed by treatment with ferric chloride (see Runs 424 and 425).

To achieve a more economical regeneration procedure, two approaches were investigated. Sorbents 415 (Run 425) and 413 (Run 426) were regenerated with portions of a used ferric chloride solution collected from a previous regeneration. Due apparently to the change produced by the sodium hydroxide (Run 424), sorbent 415 regained little of its previous phosphorus capacity. Sorbent 413, however, regained 54% of its initial capacity when regenerated with approximately half the used ferric chloride solution from Run 419. This would effect a saving of 50% of the ferric chloride requirement, which was still substantial (2 mmoles/ml of wet resin, or 22 moles of Fe per mole of P). A more significant reduction in the ferric chloride requirement was achieved when sorbent 413 was regenerated with 3 g of ferric chloride (Run 427). While the amount of ferric chloride used was reduced by a factor of 18, the total phosphorus capacity of the regenerated sorbent was over one-third of that obtained with the larger amount of ferric chloride. The requirement for ferric chloride, per mole of phosphorus, was thus reduced by a factor of six (albeit at the expense of a larger resin requirement). Since the ferric chloride cost proved to be the largest item in the cost estimate (vide infra), the process using the lesser amount of ferric chloride was adopted for economic reasons.

TABLE 23

REGENERATION OF A200/Fe(a)

Run	Sorbent	P Capacity, 1st Exhaustion mg/ml wet resin	Regenerant	P Capacity, 2nd Exhaustion mg/ml wet resin	P Capacity, 3rd Exhaustion, mg/ml wet resin
395A	390A(b)	0.52	$FeCl_3$(c)	0.35	--
395B	390B(b)	0.52	$HCl/FeCl_3$(d)	0.17	--
395C	390C(b)	0.52	HOAc(e)	0.17	--
395D	390D(b)	0.52	$NH_4OH/HOAc$(f)	0.17	--
401A	398A(b)	0.70	$FeCl_3$(c)	0.35	0.35
401B	398B(b)	0.69	$HCl/FeCl_3$(d)	0.34	0.34
401C	398C(b)	0.70	HOAc(e)	0.35	0.17
401D	398D(b)	0.70	$NH_4OH/HOAc$(f)	0.17	0.17
404A	403A(g)	0.70	$FeCl_3$(c)	0.52	--
404B	403B(g)	0.52	$FeCl_3$(h)	0.53	--
404C	403C(g)	0.70	$FeCl_3$(i)	0.34	--

(a) P Capacities determined by Test Procedure 1 on 2.3-ml (wet) samples.
(b) Prepared by the Column Process.
(c) 100 ml of 0.1 M $FeCl_3$.
(d) 100 ml of 5% hydrochloric acid followed by 100 ml of 0.1 M $FeCl_3$.
(e) 100 ml of 6% acetic acid.
(f) 100 ml of 1.0 M ammonium hydroxide followed by 100 ml of 6% acetic acid.
(g) Prepared by the Drip Process.
(h) 50 ml of 0.2 M $FeCl_3$.
(i) 25 ml of 0.4 M $FeCl_3$.

TABLE 24

REGENERATION OF A200/Fe BY THE COLUMN PROCESS(a)

Run	Sorbent	P Capacity 1st Exhaustion	Regenerant	P Capacity 2nd Exhaustion	P Capacity 3rd Exhaustion
410A	410A(b)	1.35	$HCl/FeCl_3$(c)	8.68	8.42
410B	410B(b)	1.48	$FeCl_3$(d)	8.27	7.06
414C	409A(b)	1.18	$FeCl_3$(d)	9.50	-

(a) 4.6-ml samples of sorbent were exhausted in 0.9 to 1.0-cm (ID) columns by Test Procedure 3. The sorbents were regenerated by the Column Process and exhausted in the same column. The solution used contained 25 mg P/l., except that the 1st exhaustion of 409A was done using 8 mg P/l.

(b) Prepared by the Batch Process.

(c) 100 ml of 5% HCl, then 50 ml of 0.2 M $FeCl_3$.

(d) 50 ml of 0.2 M $FeCl_3$.

TABLE 25

PHOSPHORUS CAPACITY OF A200/Fe SORBENTS ON SECONDARY EFFLUENT[a]

Run	Sorbent	Regenerant	P Capacity, mg P/ml wet resin (orthophosphate)	P Capacity, mg P/ml wet resin (total phosphate)
412	412[b][c]	-	1.74	(d)
413	413[e][f]	-	1.25	(d)
415	415[c][e]	-	1.70	(d)
419	413[g]	$FeCl_3$[h]	1.95	2.75
420	415[c]	$FeCl_3$[h]	1.72	(d)
424	415[c]	NaOH[i]	nil	(d)
425	415[c]	$FeCl_3$[j]	0.38	(d)
426	413[g]	$FeCl_3$[k]	1.34	1.63
427	413[g]	$FeCl_3$[l]	0.85	1.11

(a) 46-ml lots of sorbent were evaluated by Test Procedure 3, using chlorinated secondary effluent obtained from the Whittier Narrows Water Reclamation Plant. Lots of effluent were kept for a maximum of two days, during which the pH varied between an initial 7.3 to 7.4 and a final pH of 8.3 to 8.4 (no attempt was made to control pH). The orthophosphate content averaged 6.2 mg P/l., and the total phosphate content averaged 9.8 mg P/l.

(b) Prepared by the Batch Process.

(c) Evaluated in a 3.0-cm (ID) column at 3.0 ml/min.

(d) Not determined.

(e) Prepared by the Column Process.

(f) Evaluated in a 3.6-cm (ID) column at 3.0 ml/min. This ID apparently resulted in a bed of insufficient depth.

(g) Exhausted in a 2.5-cm (ID) column at 2.1 ml/min.

(h) Regenerated in the 3.0-cm column with 1.0 l. of 0.2 M $FeCl_3$.

(i) Regenerated with 200 ml of 0.1 N sodium hydroxide.

(j) Regenerated with 200 ml of used $FeCl_3$ solution from Run 420.

(k) Regenerated with 500 ml of used $FeCl_3$ solution from Run 419.

(l) Regenerated with 30 ml of a 10 wt-% solution of $FeCl_3 \cdot 6H_2O$ at 1.0 ml/min.

TABLE 26

PHOSPHORUS REMOVAL FROM SECONDARY EFFLUENT BY A200/Fe SORBENT

Fraction	Volume, ml	Total P Concentration, Secondary Effluent mg/l	Total P Concentration in Product, mg/l	mg P Removed
419-1	1000	9.55	0.00	9.55
419-2	1295	9.55	0.00	12.37
419-3	1000	11.37	0.00	11.37
419-4	1800	11.37	0.00	20.47
419-5	1000	11.37	0.01	11.37
419-6	1660	11.37	0.00	18.87
419-7	1000	11.37	0.04	11.37
419-8	1610	11.95	0.07	19.24
419-9	1000	11.95	0.48	11.95
419-10	1000	11.95	0.49	
419-11	1680	7.89	0.82	

Total mg P removed = 126.56.

Total P Capacity = 126.56/46 = 2.75 mg P/ml wet resin.

It was found that spent regenerant solutions could be treated with lime to remove both the ferric chloride and the eluted phosphate. Aliquots of spent regenerant (approximately 0.2M in ferric chloride) were treated with 1, 2, and 3 equivalents of calcium hydroxide. After filtration, analysis of the filtrates by the extraction modification of the stannous chloride procedure (Reference 23) showed that 99.9% of the phosphate was removed, along with virtually all of the iron (K_{sp} for $Fe(OH)_3$ is 1.5×10^{-36} – Reference 24).

On the laboratory scale, then, the present optimum version of this phosphorus removal process consists of converting A200/Na to its iron (III) form by treatment with 1.17 g of ferric chloride ($FeCl_3 \cdot 6H_2O$) per ml of wet resin. The resin is exhausted at a flow rate of 0.5 gal/min/ft^3. Regeneration is accomplished with 0.065 g of ferric chloride per ml of wet resin. Product water is used for backwashing and rinsing. Iron and phosphorus are removed from spent regenerant solutions by treatment with lime, with the resulting sludge being transferred to settling tanks for final disposal.

One aspect of this sorption process is particularly noteworthy. Examination of the total phosphorus concentration data for the product water in Run 419 reveals that the first eight fractions, totaling 90% of the reported phosphorus capacity, had product concentrations of 0.07 mg P/l. or less. Dryden and Stern have reported (Reference 25) that algae growth is inhibited in effluent containing phosphate concentrations of 0.16 mg P/l. or less. Effluent from the A200/Fe sorption process clearly fulfills the need for reducing phosphorus content below this level. An estimate of the cost of accomplishing phosphorus removal by this method is discussed in the following section.

ECONOMIC ANALYSIS

Introduction

One objective of this program was the preparation of cost estimates for methods developed in the laboratory, assuming that such methods will be used for phosphate removal from the secondary effluent of a one million gallon per day municipal sewage plant. The method investigated in the laboratory showed that the cation exchanger/metal salt sorbent – Amberlite 200/Fe sorbent – has a high phosphate capacity. The economics of this system, as developed in the laboratory, was determined. An optimized system, the feasibility of which has not yet been proved, is also discussed.

Operating and Design Conditions

Table 27 gives the general operating and design conditions for removal of phosphate from one million gallons per day of secondary effluent. It is assumed that the total phosphate will be reduced 98.4%, from 10 mg P/l. to <0.16 mg/l.

TABLE 27

DESIGN CONDITIONS FOR PHOSPHATE REMOVAL FROM SECONDARY EFFLUENT USING CATION EXCHANGER/METAL SALT SORBENT

(1,000,000 gpd Sewage Treatment Plant)

Resin Capacity, mg P/ml resin @ 0.5 gpm/cu ft resin	1.0[(a)]
Secondary Effluent Exhaustion Cycle Rate, gpm	760
Quantity Amberlite 200 Resin, cu ft	1,520
Effluent Treated at Resin Capacity, million gal.	1.0
Exhaustion Cycle, hours	22
Resin Depth, ft	6.1
Vessel ID, ft	12.5[(b)]
Vessel Area, Total sq ft	245
Flow Rate, gpm/sq ft	3.1
Pressure Drop, psi	1.5
Backwash, @ 8 gpm/sq ft for 10 min, gal.	19,600
Regenerant, $FeCl_3$ (as 100%), ton/cycle	1.63
Regenerant, gal. H_2O/cycle	19,800
Lime (90% CaO), lb/cycle	2,320
Regeneration Time, min/cycle @ 0.5 gpm/cu ft	≃30
Rinse Water, gal/cycle @ 50 gal/cu ft	75,000
Rinse Time, min/cycle @ 1 gpm/cu ft	50
Feed Tank, gal. hold-up during clean-up	168,000

(a) Assumes capacity of 2.75 mg P/ml resin with residue of 1.75 mg P/ml left on resin after regeneration.

(b) Two tanks required.

Design conditions are given for a flow rate of 0.5 gpm per cu ft Amberlite 200 resin. The 0.5 gpm per cu ft resin rate provided zero phosphate leakage under the experimental conditions with a resin capacity of 2.75 mg P/ml resin.

The ferric chloride required for regeneration is still high for an economical system. It would be expected, however, that additional experimental work would significantly reduce the ferric chloride requirement.

The cycle, consisting of a long exhaustion period and short regeneration time, would be ideally suited to continuous countercurrent systems that are offered in the ion exchange field. A single cell concept, however, was considered to be more economical wherein the flow through the bed would be semi-continuous, requiring shutdown of the system during backwash, regeneration, and rinsing periods. The system is shown in the Flow Diagram, Figure 2.

The secondary effluent flows from the existing final clarifier to the secondary effluent feed tank. During the exhaustion cycle, the secondary effluent is pumped from the feed tank through the phosphate exchanger cell with the purified effluent being discharged to the product water storage tank. (The feed tank also serves as an accumulator for secondary effluent during backwash, regeneration, and rinse periods.) The overflow from the product water storage tank becomes the essentially phosphate-free sewage plant effluent.

The product water is used to backwash the phosphate exchanger. This stream is then discharged to the final clarifier where any suspended solids (removed from the top of the exchanger bed) settle out with the solids contained in the secondary effluent.

Product water can also be used to make up the regenerant, ferric chloride solution. This solution is circulated through the exchanger and removes the accumulated phosphates. A side stream is removed to the slurry tank where it is reacted batchwise with lime, resulting in a precipitate of ferric hydroxide and hydroxylapatite. This slurry is then pumped to a separate sedimentation tank from which the solids can be removed for disposal.

Product water is also used for rinsing the resin bed. This rinse water, contaminated with ferric chloride and other residues, is either discharged to the slurry tank or it can be used as make-up water for fresh ferric chloride solution.

Cost Estimate

Cost estimates were prepared for the system described above. The OSW guideline (Reference 26) provided the basis and technique for these estimates. A rough-order-of-magnitude capital cost estimate was made as shown in Table 28. This capacity is not utilized in the proposed system,

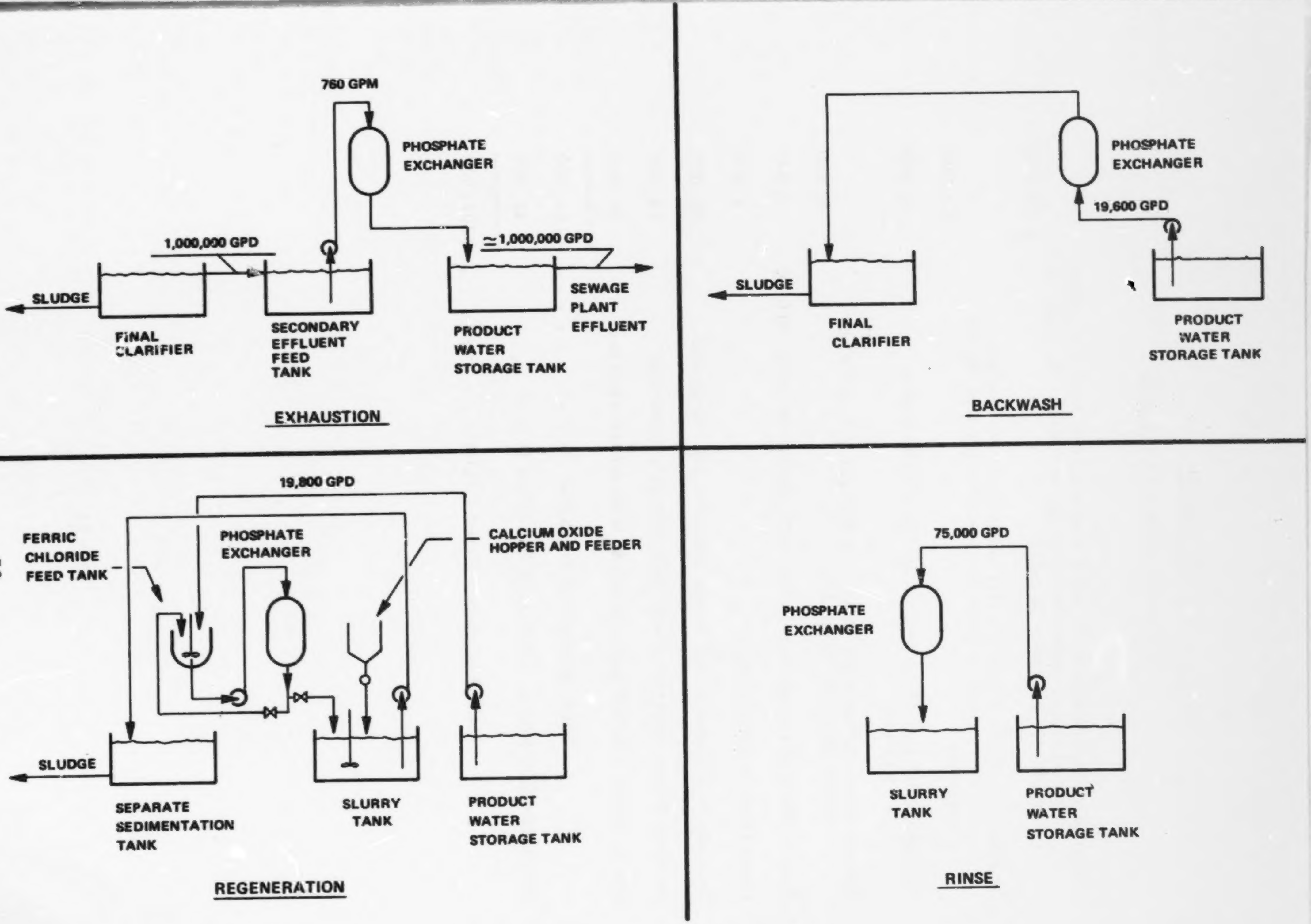
760 GPM
PHOSPHATE EXCHANGER
1,000,000 GPD
≃1,000,000 GPD
SLUDGE
FINAL CLARIFIER
SECONDARY EFFLUENT FEED TANK
PRODUCT WATER STORAGE TANK
SEWAGE PLANT EFFLUENT
EXHAUSTION
PHOSPHATE EXCHANGER
19,600 GPD
SLUDGE
FINAL CLARIFIER
PRODUCT WATER STORAGE TANK
BACKWASH
19,800 GPD
FERRIC CHLORIDE FEED TANK
PHOSPHATE EXCHANGER
CALCIUM OXIDE HOPPER AND FEEDER
SLUDGE
SEPARATE SEDIMENTATION TANK
SLURRY TANK
PRODUCT WATER STORAGE TANK
REGENERATION
75,000 GPD
PHOSPHATE EXCHANGER
SLURRY TANK
PRODUCT WATER STORAGE TANK
RINSE

FIGURE 2. FLOW DIAGRAM - PHOSPHATE REMOVAL FROM SECONDARY EFFLUENTS USING CATION EXCHANGER/METAL SALT SORBENT

TABLE 28

CAPITAL COST ESTIMATE

Phosphate Exchanger Cell, 12.5 ft dia x 10 ft high st. sides, rubber-lined steel with piping, accessories, and automatic controls (2 cells)	$ 60,000
Regenerant Tank, 30,000 gal., 23 ft dia x 10 ft high, steel with baked phenolic resin lining and 30 HP agitator	18,000
Pumps, 1000 gpm @ 60 psig, 316 SS, 25 HP motor (2 required)	9,000
Ferric Chloride Storage Tank, 15,000 gal., steel with baked phenolic resin lining	8,000
Ferric Chloride Transfer Pump, 100 gpm @ 60 psig, 316 SS	3,000
Lime Hopper and Feeder	8,000
Secondary Effluent Feed Tank, 200,000 gal. concrete	20,000
Product Water Storage Tank, 120,000 gal. concrete	14,000
Slurry Tank, 40,000 gal. concrete with 60 HP agitator	20,000
Total Equipment Installed	$160,000
Amberlite 200 Resin, 1520 cu ft @ $28/cu ft	42,500
Total Estimated Fixed Capital	$202,500

however, since the ferric chloride requirement for total regeneration is very high. Experimental conditions under which only partial regeneration was accomplished were chosen to reduce the ferric chloride cost. Under these conditions, the spent resin containing 2.75 mg P/ml is treated with only enough ferric chloride to remove 40% of the phosphorus from the resin. Thus, the net capacity of the resin is 1 mg/ml. This results in a relatively large volume of resin which, however, is lower in cost than the indicated quantity of ferric chloride needed for complete regeneration.

Table 29 outlines the annual cost basis. It is assumed that the facility would have a 30-year life and that financing would be done by issuing a 30-year municipal bond. The cost of borrowing money has been rising rapidly during the last few years. Selection of a fair interest rate is important, since the rate can be a substantial part of the total annual operating cost. An average interest rate of 4-1/2% is assigned to this project which is considered to be a conservative figure during the total amortization period. The total carrying charge factor consists of this interest rate plus the corresponding sinking fund factor required to pay for the equipment.

The capital costs and amortization of replaceable items and resin are calculated as two separate items, since they are considered to have shorter useful lives. Replaceable items are assumed to have a 10-year life, while resin will have to be replaced every five years. The appropriate sinking fund factor is applied to each category in addition to the interest. Only interest is applied to the working capital, since the working capital will be recovered at the end of the project life. Derivation of working capital is shown in Table 30.

The estimated costs are summarized in Table 31. It will be noted that the ferric chloride cost is the highest single cost item, contributing about 13¢/1000 gal. (Kgal) of effluent treated. In this case, the ferric chloride usage is equivalent to an 8:1 molar ratio of ferric ion to phosphorus.

It would be expected that additional experimental and development work would result in cost reductions in an optimized system. Improvement in resin capacity would reduce both capital cost and resin replacement cost. Improvements in regeneration would reduce ferric chloride costs. For example, reducing the molar ratio of ferric ion to phosphorus to 2:1 would reduce costs by more than 9¢/1000 gal. effluent treated. With the various improvements that might be possible, an optimized system could probably operate at a cost approaching 20¢/1000 gal. effluent.

TABLE 29

ANNUAL COST BASIS

Plant Capacity Factor: 90%, 330 days/year; 7920 hours/year.

Carrying Charges

	Plant	Replaceable Items	Resin
Lifetime, years	30	10	5
Interest, %	5.0	0.25	0.25
Sinking Fund Factor, %	1.505	10.00	20.00
Carrying Charge Multiplier, %	6.505	10.25	20.25

Recurring Costs

Taxes: 2% fixed capital	$ 4,050/year
Insurance: 1% fixed capital	$ 2,030

Labor

Operating: 8 hr/cycle @ $4.00/hr	$ 8,000/year
Supervisory: 15% of operating labor	1,200/year
Maintenance: 2.5% of fixed capital (-resin)	4,000
Total	$13,200

Supplies and Maintenance Materials

2% of fixed costs (-resin)	$ 3,200/year

General and Administrative

Payroll Burden, 20% of total labor	$ 2,640/year
Plant Overhead, 50% of total labor, maintenance and supplies	$ 8,200/year

TABLE 29 (Continued)

Chemicals			
Ferric Chloride (as 100%), 538 tons @ $80/ton			$43,040/year
Lime, 383 tons @ $18/ton			$ 6,890/year
Resin 200, 304 cu ft @ $28/cu ft			$ 8,510/year
Utilities			
Power: 265,000 kwh @ 10 mills			$ 2,650/year
Replaceable Items (10-year life)			
Pumps	$12,000		
Agitators	9,000		
Feeder	3,000		
Automatic Controls	5,000		
Total	$29,000	or	$ 2,900/year

TABLE 30

WORKING CAPITAL

	Dollars
Chemical Inventory, 2 months	$ 9,750
Labor, 3 months	3,300
Payroll Burden, 3 months	660
Plant Overhead, 4 months	2,730
Fixed Cost, 0.5% of fixed capital	1,010
Spare Parts and Miscellaneous, 1% of fixed capital	2,020
Total	$19,470

TABLE 31

COST SUMMARY

Phosphate Removal System for 1,000,000 gpd Secondary Effluent

Capacity Factor: 0.90 Output: 330,000 K gal/yr

Interest Rate: 4-1/2% Plant Life: 30 years

	Capital Cost Dollars	Carrying Charge	Annual Cost, $	Treating Cost	
				¢/K gal	%
CAPITAL COSTS					
1. Fixed Capital (30-yr bond)	131,000	0.0614	8,040	2.44	7.1
2. Replaceable Items (10 yr)	29,000	0.0814	2,360	0.72	2.1
3. Resin (5 yr)	42,500	0.1828	7,770	2.35	6.8
4. Working Capital	19,470	0.0450	880	0.26	0.8
Total Capital Costs	221,970				
RECURRING COSTS		%			
5. Taxes		2	4,050	1.22	3.5
6. Insurance		1	2,030	0.62	1.8
Total Annual Fixed Costs			25,130	7.61	22.1
OPERATING AND MAINTENANCE COSTS					
7. Operating Labor			8,000	2.42	7.1
8. Supervisory Labor			1,200	0.36	1.0
9. Maintenance Labor			4,000	1.21	3.5
10. General and Administrative			10,840	3.29	9.6
11. Supplies and Maintenance Materials			3,200	0.97	2.8
12. Ferric Chloride			43,040	13.04	37.9
13. Lime			6,890	2.09	6.1
14. Resin			8,510	2.58	7.5
15. Power			2,650	0.81	2.4
16. Other			-		
Total Operation and Maintenance Costs			88,330	26.77	77.9
TOTAL FIXED PLUS O&M COSTS			113,460	34.38	100.0

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SECTION IV

EXPERIMENTAL PROCEDURES

SORBENT SYNTHESIS

Resin Sulfonyl Chloride

Dowex 50W-X8 (H) (50 g wet weight, 46% solids) was stirred with 200 ml of 50% (vol) H_2SO_4 solution at room temperature for 1 hr. The acid was removed with a filter stick and the procedure was repeated successively with 80%, 95%, and 100% H_2SO_4. The beads were placed in a 200-ml 3-neck flask fitted with a paddle stirrer, thermometer with Therm-o-Watch control (I^2R Company, Cheltenham, Pennsylvania), and drying tube. $ClSO_3H$ (150 ml) was added (some gas evolution) and the mixture was stirred for 1 hr. The acid was replaced with fresh $ClSO_3H$ and the mixture was stirred overnight at room temperature and then at 80° for 6 hr. The contents were cooled and the liquid removed with a filter stick. The beads were washed on the filter (no suction) with the following: chloroform; dioxane (and overnight standing); acetone (and 1-hr standing); ice water; and 5% Na_2CO_3 (0°). The beads were then soaked at 0° for 1 hr, first with 5% Na_2CO_3 (the final pH was alkaline), and then with water (neutral pH). After standing for 1 hr in acetone, the beads were air-dried, and then warmed for 3 hr at 40° (3 mm). The dark brown, unfractured beads remained odor-free and unchanged in appearance during 3 weeks of surveillance, at which time a faint HCl odor was detected.

The extent of conversion of RSO_3H to RSO_2Cl was determined by elemental analysis for chlorine and by direct titration of RSO_2Cl. The former gave 14.6% Cl (theory, 16.3), corresponding to an 89.5% conversion. The latter (performed by immersion of the sample in excess 0.1 N NaOH for 3 days, followed by back titration with 0.1 N HCl) indicated a chlorine content of 16.0%, or a 98.3% conversion. The smaller (elemental analysis) value was preferred because of the known imprecisions of the titration procedure.

Resin Carbonyl Chloride

In a 300-ml 3-neck flask fitted with a paddle stirrer, thermometer, and reflux condenser topped by a drying tube were placed 10.9 g (0.12 eq) of dry IRC-50 resin and 90 ml of dry toluene. The mixture was stirred at 90-95° for 1.2 hr, cooled to room temperature, and 46.3 g (0.22 mole) of PCl_5 was added. The contents were stirred at 110° for 20 hr (HCl evolution was noted). The beads were washed repeatedly with toluene and then with methylene chloride (stirring, soaking for 1 hr, and decantation). After removal of solvent in vacuo and drying for 4 hr at 50° (3 mm), 11.2 g of intact, light tan beads were obtained, which did not develop an odor of HCl on standing.

The resin contained 10.0% Cl (theory, 32.4), and the presence of strong absorptions at 1820 and 1760 cm^{-1} in the infrared indicated a significant anhydride content. The apparent discrepancy between the slight weight increase and the significant chlorine content is probably due to a weight loss (such as organic sloughage) occurring during the reaction.

ES-1 Copolymer

In a 500-ml resin kettle fitted with a stainless steel stirrer (3-in. propeller), reflux condenser, nitrogen inlet tube extending below the liquid, and oil bath, were placed 300 ml of water, 2.0 g of polyvinyl alcohol (Matheson, Coleman and Bell — 99% hydrolyzed; viscosity of 4% solution at 20°, 28-32 cps), and 1.0 g of magnesium silicate. The mixture was stirred at 85° (oil bath temperature, Matheson Lab-Stat temperature control) for 30 minutes while nitrogen was bubbled through at a fast rate. The heat was removed, and when the temperature had dropped to 60°, the nitrogen inlet tube was replaced with static nitrogen pressure applied to the top of the condenser. A solution of 0.5 g of benzoyl peroxide in 50 ml of distilled styrene and 0.8 g of technical DVB (62% DVB, 38% ethylstyrene) was added, the stirrer speed adjusted to 800 rpm, and the suspension stirred at 85° (oil bath temperature) for 6 hr. Stirring was continued while the mixture cooled. After the decantation of some floating granules, the beads were strained through a 100-mesh sieve, washed three times with water and three times with methanol, and left to stand in methanol overnight. The methanol was removed by suction, and the beads were dried in air, and then for 3 hr at 45° (3 mm). The yield of hard, almost transparent, beads was 25 g, 80% of which were of 45-100 mesh and 20% of 20-45 mesh.

ES-1 Chloromethyl Resin

In a 100-ml 3-neck flask fitted with paddle stirrer, reflux condenser, and drying tube, were placed 4 g of ES-1 copolymer (45-100 mesh), 40 g of chloromethyl methyl ether, and 3 g of ground, anhydrous zinc chloride (previously melted and cooled in a desiccator). After being stirred for 1 hr at room temperature and for 2 hr at reflux, the beads were filtered off, washed with methylene chloride, and left overnight in that solvent. They were then rinsed with cold water and finally with acetone. After drying in air and for 3 hr at 45° (3 mm), 5.24 g of intact, light yellow beads were obtained. The chlorine content was 27.2%, indicating the substitution of 1.15 CH_2Cl groups per aromatic ring.

Sorbitol Sodium Salt

A 500-ml, three-neck flask fitted with mechanical stirrer and drying tube was flamed out, flushed with nitrogen, and cooled with a dry ice-acetone bath. Into the flask were introduced 250 ml of liquid ammonia, and after replacing the drying tube with a static nitrogen pressure, 25 g (0.14 mole) of sorbitol and 3.2 g (0.14 g-atom) of sodium. The dark blue mixture soon decolorized. After 15 min stirring, the cooling bath was removed, and most of the ammonia was driven off by warming the stirred contents of the flask (hot-air gun) for 3.5 hr. At this time, a Nessler test was strongly positive (orange color and precipitate), although ammonia was not detectable by odor or by reaction with HCl vapor. The white powder was heated at 120° (3 mm) for 3 hr. The fractured plates (28.0 g) obtained from the molten layer of sorbitol sodium salt gave a weakly positive Nessler test (faint yellow color). Studies by Chablay (Reference 27) indicate that the reaction yields the monosodium salt of the polyol.

Resin Pyrogallyl Sulfonate

In a 250-ml flask equipped with paddle stirrer, condenser, drying tube, and thermometer were placed 4.34 g (19.5 mmoles) of D50W sulfonyl chloride (15.8% Cl, 97.1% converted), 3.78 g (30 mmoles) of pyrogallol, 2 ml (25 mmoles) of pyridine, and 45 ml of dry DMF. The mixture was stirred for 1 hr at room temperature and then heated to 75° over a period of 30 min. Stirring was continued for 4.5 hr at 75 to 80°. After standing overnight, the contents were added to an ice/dilute HCl mixture. The beads were washed by repeated swirling and decantation (30 min) until no odors of pyridine or DMF could be detected. The beads were soaked and rinsed with several portions of acetone (40 min) to remove water. After removal of most of the acetone at the water pump, the product was dried at 45 to 50° (3 mm) for 3 hr. The weight gain was 1.01 g, 58.1% of theoretical. The product contained 10.90% S; the calculated value, for a 58.1% converted product was 11.95%. Qualitative tests for chloride were weakly positive. (Later preparations of the pyrogallyl sulfonate, similarly performed, contained only 0.5 to 0.8% Cl). Strong infrared absorptions at 1200, 1630, 1540 and 1485 cm^{-1} indicated the presence of a catechol derivative.

Resin Mannityl Sulfonate (DMF/Triethylamine Method)

In a 50-ml Erlenmeyer flask fitted with magnetic stirrer, condenser, and drying tube were placed 2.5 g (10.5 meq) of D50W sulfonyl chloride and 20 ml of dry DMF. After stirring at room temperature for 1 hr, 2.1 g (11.5 meq) of mannitol and 5 ml triethylamine were added. The mixture was then stirred at 100° for 4 hrs. The warm solution was decanted; the beads were washed with water, transferred to a column, and further washed by the passage of 200 ml of water (2 hr) and 300 ml of acetone (2 hr). The product was dried in air and then at 40° for 3 hr (3 mm). The beads weighed 3.1 g, and contained 10.7% S, 2.0% Cl, and 4.6% N. The infrared spectrum had strong OH and CH_2 absorptions (mannitol) and a trace of carbonyl (DMF). When the beads were rinsed with a 2% NaOH solution, a strong amine odor was detected. Although the weight of the product corresponded to a 41% conversion to the mannityl ester, the actual conversion was somewhat less, because of the presence of the amine, as sulfonate salt or sulfonamide, and the small amount of DMF.

Resin Mannityl Sulfonate (Mannitol Sodium Salt Method)

In a 100-ml, 3-neck flask fitted with paddle stirrer and nitrogen inlet were placed 25 g of mannitol, 3 g (15 meq) of ES-1 sulfonyl chloride, 4.6 g (22.5 mmoles) of mannitol sodium salt, 2.2 g (15 mmoles) of sodium iodide, 8 ml of bis [2-(2-methoxyethoxy)ethyl] ether, and 10 ml of toluene. The reaction mixture was stirred at 180° overnight (Matheson Lab-Stat control) under a stream of nitrogen. The mixture was then cooled to 100°, the polyol dissolved in hot water, the beads separated, washed with water, stirred in water for 1 hr, washed with acetone, air dried, then vacuum dried for 3 hr at 45° (3 mm). The yield of dark-brown, intact beads was 3.31 g, or 14.4% of theory based on the weight increase.

Resin N-Methylglucamyl Sulfonamide

In a 100-ml 3-neck flask fitted with paddle stirrer, reflux condenser and drying tube were placed 5 g (19.8 meq) of A200 sulfonyl chloride, 8.5 g (43.5 meq) of NMG, 40 ml of dioxane, and 4 ml of water. After stirring at reflux temperature for 3 hr, the beads were thoroughly washed with water, stirred in 2% HCl solution for 1 hr, rinsed with water, immersed in water for 1 hr, and rinsed with acetone. After standing in acetone for 1 hr, the beads were dried in air and then for 3 hr at 45° (3 mm). The grey beads weighed 6.48 g; the gain in weight (1.48 g) was 47.2% of theory. Analysis indicated 1.07% Cl and 2.28% N; the theoretical nitrogen content for 100% conversion was 3.40%.

Resin N-Methylglucamyl Carboxamide

In a 250-ml flask equipped with paddle stirrer, condenser, drying tube, and thermometer were placed 3.0 g of IRC-50 chloride/anhydride, 9.0 g of NMG, and 40 ml of DMF. The mixture was stirred at room temperature for 1.5 hr, permitted to stand overnight, and then stirred for 10 hr at 90-105°. The supernatant was decanted and the product was stirred with several portions of 2% HCl solution (25 min). The acid was removed by repeated washing with water. The beads were soaked in several portions of acetone to remove water, dried at the water pump, and then warmed at 50° (3 mm) for 3 hr. The weight gain was 2.57g, or 59.2% of theoretical. Analysis indicated 3.92% N (theory, for a completely reacted product, 5.22% N). No residual chlorine was present.

Resin Sorbityl Ether

In a 100-ml 3-neck flask fitted with paddle stirrer and nitrogen inlet were placed 25 g of sorbitol, 3.3 g (25 meq) or chloromethylated ES-1 copolymer, 8 ml of bis(2-methoxyethyl)ether, 10 ml of toluene, 4.1 g (27.5 mmoles) of sodium iodide, and 6.5 g (32 mmoles) of sorbitol sodium salt. The reaction mixture was stirred under a stream of nitrogen at 130° for 16 hr. The mixture was cooled to 100° and the solids were added to hot water. The beads were successively washed with water, stirred in water for 1 hr, washed with acetone, and air dried. After further drying for 3 hr at 45° (3 mm), the yield of intact yellow beads was 5.0 g, or 41.3% based on the weight increase. The infrared spectrum contained strong absorptions in the ether region (1040-1100 cm^{-1}).

Resin/Metal Sorbents (Batch Process)

To 11.5 ml (wet volume, 22 meq) of A200/Na was added 500 ml of 0.1 M aqueous ferris chloride solution. The suspension was stirred gently for 2 hours at room temperature, and the solution was decanted. The beads were washed several times with water, by decantation, and were stored wet. Analysis of one such preparation (after drying) showed that the beads contained 0.20% Cl and 10.0% Fe.

Resin/Metal Sorbents (Drip Process)

A 2.3-ml portion (wet volume, 4.4 meq) of A200/Na was placed in a 20 x 45-mm glass funnel equipped with a coarse fritted disc. The resin was washed several times with deionized water and covered with a disc of filter paper. A fresh 0.2 M solution of ferric chloride was prepared by dissolving 2.7 g (0.01 mole) of $FeCl_3 \cdot 6\,H_2O$ in 50 ml of water. The ferric chloride solution was added from a dropping funnel at 1.4 + 0.1 ml/min. The sorbent was washed thoroughly with water on the filter and stored wet until used.

Resin/Metal Sorbents (Column Process)

A 3.0-cm (ID) chromatographic column equipped with a teflon stopcock was plugged with a small amount of glass wool. Enough 1/8-in. beads were added to reach a depth of 1-in., and water was added to a depth of 6- to 8-in. A slurry of 46 ml (wet volume, 88 meq) of A200/Na in water was poured in, and most of the water was drained off. The resin beads were classified by backwashing with water, at a rate which produced at least a 50% expansion of the resin bed. After draining the water to a depth of 2 to 5 cm above the resin, a plug of glass wool was placed in the column approximately 1 cm from the top of the resin bed. A dropping funnel was connected to the column by means of plastic tubing and a rubber stopper. A freshly prepared solution of ferric chloride (1.0 l., 0.2 M) was added from the dropping funnel at a rate of 3.0 + 0.2 ml/min by adjusting the column stopcock to that rate with the dropping funnel stopcock in the open position. After addition of ferric chloride, the sorbent was washed with 500 ml of water at the same rate, followed by 2 to 3 l. of water over a period of 30 min. The sorbent was stored under water until analyzed.

SORBENT EVALUATION

Phosphorus Capacity (Test Procedure 1) – (Used for the evaluation of XE-243 and resin/metal sorbents)

All glassware was rinsed twice with warm 5% HCl solution and with distilled water prior to use. An amount of wet sample corresponding to 2 g of dry resin (for XE-243) or 1 g of dry resin (for resin/metal sorbents) was placed in a 20 x 45-mm Pyrex funnel equipped with a coarse fritted disc. After repeated washings with distilled water, the resin was covered with a disc of filter paper and standard Na_2HPO_4 test solution (8.16 mg P/l.; 500 mg NaCl/l.) was added dropwise from a calibrated dropping funnel at 1.4 + 0.1 ml/min. Effluent was collected in 50-ml aliquots until the breakthrough concentration of 0.326 mg P/l. was reached. Phosphorus analyses were made with the standard stannous chloride-ammonium molybdate procedure (Reference 23). Determination of the phosphorus concentrations in the effluents permitted the calculation of the amount of phosphorus retained in the sorbent.

Regeneration was accomplished by first rinsing the resin bed to remove adhering test solution and then adding the regenerant (100 ml of 5% H_2SO_4 solution for XE-243 samples and 200 ml of 0.1 M $FeCl_3$ solution in the case of resin/metal sorbents) at the dropwise rate of 1.4 + 0.1 ml/min. The stripped sorbents were rinsed with water prior to further cycling.

Phosphorus Capacity (Test Procedure 2)

For the evaluation of polyol sorbents, the above procedure was modified as follows: (a) 2 g (dry weight) of sample was taken; (b) the rate of addition of test solution was 1.0 + 0.1 ml/min; and (c) 25-ml aliquots of effluent were collected. Regeneration studies were not made because of the low capacity of these sorbents.

Phosphorus Capacity (Procedure 3)

Sorbent columns were prepared and classified as described in the Column Process for sorbent preparation. For 4.6-ml samples, burets having an ID of 0.9 to 1.0 cm and equipped with Teflon stopcocks were used. Columns of 2.5 and 3.0-cm ID were used for larger scale work. Phosphate solution, 8.16 or 25 mg P/l., was added from a reservoir connected to the column by plastic tubing. Effluent was released from the column at 0.25 ml/min for the burets, 2.1 ml/min for the 2.5-cm column, and 3.0 ml/min for the 3.0-cm column. Effluents were collected in suitable aliquots for phosphorus analysis.

SECTION V

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SECTION VI

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SECTION VII

GLOSSARY*

A200	Amberlite 200, sulfonic acid resin, 20% DVB (Rohm and Haas Co.)
D50W	Dowex 50W-X8, sulfonic acid resin, 8% DVB (Dow Chemical Co.)
DMF	N, N-Dimethylformamide
DMSO	Dimethyl sulfoxide
DVB	Divinylbenzene
ES-1	Styrene-Divinylbenzene copolymer, 1% crosslinked
ES-1S	ES-1 sulfonic acid resin
IR-118	Amberlite IR-118, sulfonic acid resin, 5% DVB (Rohm and Haas Co.)
IR-120	Amberlite IR-120, sulfonic acid resin, 8% DVB (Rohm and Haas Co.)
IR-124	Amberlite IR-124, sulfonic acid resin, 12% DVB (Rohm and Haas Co.)
IRA-400	Amberlite IRA-400, trimethylammonium chloride resin, 8% DVB (Rohm and Haas Co.)
IRC-50	Amberlite IRC-50, carboxylic acid resin (Rohm and Haas Co.)
IRC-84	Amberlite IRC-84, carboxylic acid resin (Rohm and Haas Co.)
NMG	N-Methylglucamine
SDVB	Styrene-divinylbenzene copolymer
XE-243	Amberlite XE-243, N-methylglucamide resin, 1% DVB (Rohm and Haas Co.)

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*Mention of commercial products does not imply endorsement by the Environmental Protection Agency.

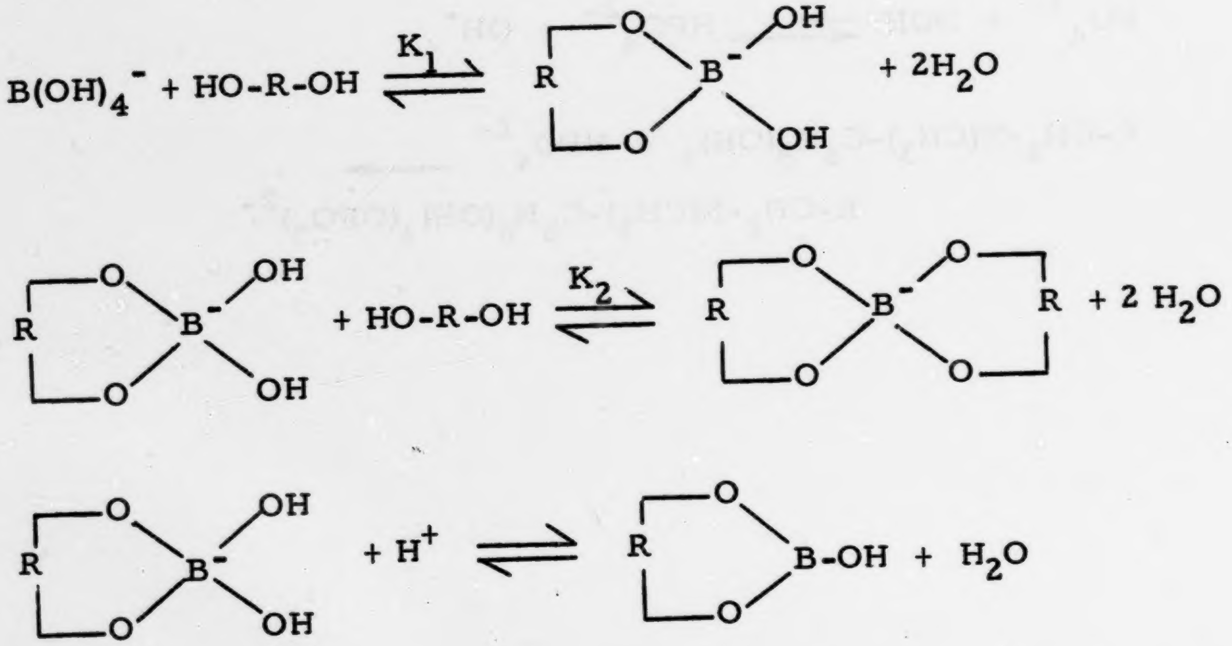
APPENDIX

INTERACTION OF PHOSPHATE WITH ORGANIC POLYOLS

The following mechanism has been advanced for the complexation of borate or boric acid with polyhydroxylic compounds such as mannitol, catechol, or pentaerythritol (Reference 1):

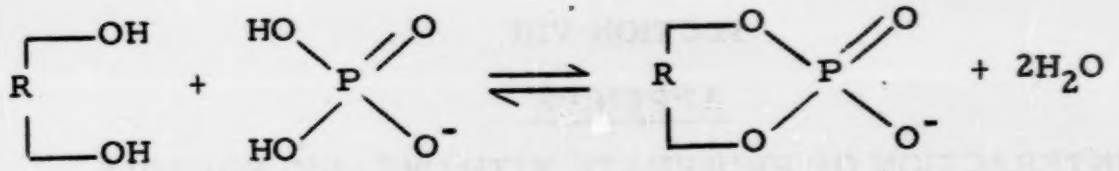
$$B_4O_7^{2-} + 7H_2O \rightleftharpoons 4H_3BO_3 + 2OH^-$$

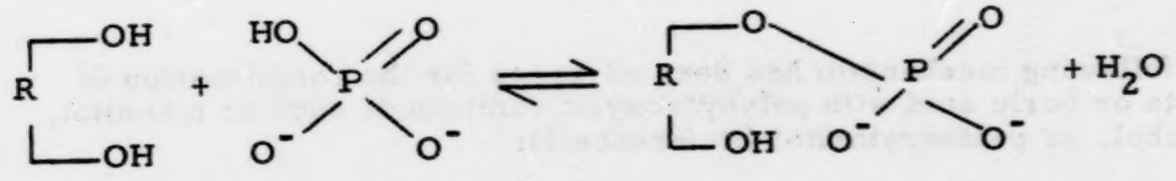
$$H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$$ (Reference 2)



Thus, the tetrahydroxyborate species, $B(OH)_4^-$, which exists in dilute solutions (0.25 Molar) of borates, may form as many as two different anionic complexes and one molecular complex with suitable polyhydroxylic compounds, under the proper conditions.

The above mechanism may be applied to the dihydrogenphosphate ($H_2PO_4^-$) and monohydrogenphosphate (HPO_4^{2-}) species as shown below.





Its application to polyphosphate ions and to the tribasic species (PO_4^{3-}) is not so easily rationalized, although it is possible that the latter, which is known to undergo sorption on XE-243, does so as the dibasic species with which it exists in equilibrium.

$$PO_4^{3-} + HOH \rightleftharpoons HPO_4^{2-} + OH^-$$

$$R\text{-}CH_2\text{-}N(CH_3)\text{-}C_6H_8(OH)_5 + HPO_4^{2-} \longrightarrow R\text{-}CH_2\text{-}N(CH_3)\text{-}C_6H_8(OH)_4(OPO_3)^{2-}$$

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27 *Abstract*

A laboratory evaluation was made of the technical and economic feasibility of phosphate removal from secondary effluent by two types of new sorption resins. Multivalent metal derivatives of sulfonic acid resins were found to have good phosphorus capacities. The iron (III) form of Amberlite 200 strong acid cation exchange resin, for example, exhibited capacities up to 9.5 mg P/ml of wet resin, and, in tests with secondary effluent, a capacity of 2.7 mg P/ml was obtained. Regeneration of the exhausted resin was readily accomplished with dilute ferric chloride solutions; ten exhaustion-regeneration cycles were performed on one sample without loss of phosphorus capacity. Iron and phosphorus were quantitatively removed from spent regenerant solutions by the addition of lime and removal of the resulting precipitate by filtration. With a second type of resin, phosphorus capacities only 25 to 30% of the commercial polyol Amberlite XE-243 were obtained. These resins included (1) polyhydroxylic esters and amides of various cation exchange resins, and (2) polyhydroxylic ethers of styrene-divinyl benzene copolymers. On the basis of the laboratory results, a phosphorus removal process was designed and a cost estimate prepared. (Wilson - Envirogenics)

Abstractor E. M. Wilson

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